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A THEORY OF THE MERCURY AMMONIA COMPOUNDS

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I. GENERAL CONSIDERATIONS

1. Introduction.—The recognition of the identity of the ammonobasic mercuric halides of the formulas NH_2-Hg-Cl,

Hg : N-Hg-Br and Hg : N-Hg-I, as prepared from liquid ammonia solutions, with the long known infusible white precipitate and the so-called dimercuriammonium bromide and iodide, respectively, brought the writer some years ago to a new point of view concerning the constitution of the members of this large and more or less obscure group of substances.[1]

Convinced, by a preliminary study of the literature, of the essential adequacy of the new theory in its application to many of the so-called mercuriammonium compounds, data concerning all known preparations of this class[2] of compounds were collected from the literature and classified with the object in view of undertaking an experimental revision of the whole field. The great San Francisco earthquake of 1906, however, put an end to this program in its beginning, and since that time other interests have intervened to prevent a continuance of the investigation.

In the interim several important contributions to the knowledge of the mercury ammonia compounds[3] have appeared, the authors of which omit entirely[4] any consideration of the theory proposed by the writer, and it is this apparent failure of an earlier and briefer presentation of the writer's theory to attract the attention of recent workers in this field which has led to the preparation of this more elaborate paper. Although at the present time the writer has no new experimental data of his own to contribute to the subject and does not see his way to take up its experimental study in the immediate future, he is, after a careful study of the papers referred to, still strongly of the opinion that his theory, at least in its fundamental outlines, explains much more satisfactorily the existence and general chemical behavior of these compounds than any others which have yet been proposed.

2. Purpose of the Article.—The object of this paper shall therefore be, first, to review briefly the several mercuriam-

[1] J. Am Chem. Soc., **27,** 835 (1905). Z. anorg. Chem., **46,** 1 (1905).

[2] J. Am Chem. Soc., **29,** 35 (1907).

[3] Strömholm: Z. anorg. Chem., **57,** 72 (1908). Widman: *Ibid.*, **68,** 1 (1910). Gaudechon: Ann. chim. phys., [8] **22,** 145 (1911).

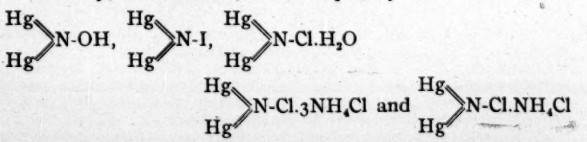
[4] Strömholm offers some objection to the separate classification of the mercury nitrogen compounds containing oxygen, but makes no reference to the theory upon which the classification is based.

monium theories which have been proposed in explanation of the nature of the mercury nitrogen compounds; second, to state with some elaboration the theory which the author proposes as a substitute for the prevailing mercuriammonium theories; third, to show that François, Strömholm, Widman and Gaudechon, in their recent experimental investigations, have contributed very material support to the author's theory; fourth, to discuss in some detail the widely accepted Rammelsberg-Pesci dimercuriammonium theory, and to present arguments which prove the untenability of this theory; fifth, to discuss the constitution of Millon's base and its dehydration and deammonation products, and to show that they are mixed compounds which are basic at the same time to both water and ammonia; sixth, to show that the numerous mercury derivatives of the acid amides find a reasonable interpretation in terms of the writer's theory.

II. THEORIES OF THE MERCURY AMMONIA COMPOUNDS

3. Current Theories.—Notwithstanding the considerable attention which has been given to the study of the mercury nitrogen compounds, widely diverse views are still held concerning their constitution, as will be evident from a consultation of the dictionaries and handbooks of chemistry, or by reference to the records of recent investigations in this field.[1]

According to the view of Rammelsberg, all the mercury ammonia compounds are referred to a single type of mercuriammonium compounds, in which the four ammonium hydrogen atoms of an ammonium salt are substituted by two atoms of mercury, as indicated, for example, by the formulas



[1] Pesci: Gazz. chim. ital., **19**, 509 (1889); **20**, 485 (1890); Z. anorg. Chem., **21**, 361 (1899). Hofmann and Marburg: Ann. Chem. (Liebig), **305**, 191 (1899); Z. anorg. Chem., **23**, 126 (1899). Fürth: Monatsh., **23**, 1147 (1902). François: Compt. rend., **130**, 332 and 1022 (1900). Franklin: J. Am. Chem. Soc., **27**, 191 (1905); **29**, 55 (1907). Strömholm: Z. anorg. Chem., **57**, 72 (1908). Widman: *Ibid.*, **68**, 1 (1910). Gaudechon: Ann. chim. phys., [8] **22**, 145 (1911).

for dimercuriammonium hydroxide and iodide, the chloride of Millon's base, or hydrated dimercuriammonium chloride, and the fusible and infusible white precipitates, respectively, which latter two compounds are thus represented as double salts of dimercuriammonium chloride and ammonium chloride.

According to other views, all the mercury ammonia compounds are formulated as substituted ammonium salts and bases, but differ from the Rammelsberg-Pesci theory in that a number of types is assumed to exist. The last three of the above enumerated compounds, for example, are in other places[1] found formulated as oxydimercuriammonium chloride, $(HgOHg)NH_2Cl$,[2] mercuridiammonium chloride, $Hg(NH_3)_2Cl_2$,[3] and mercuriammonium chloride, $HgNH_2Cl$,[4] respectively, while substances of the type of the first compounds above mentioned are formulated as dimercuriammonium compounds.

According to still other views,[5] the compounds of the type of the fusible and infusible white precipitates are removed from the category of the substituted ammonium salts and are formulated respectively as ammonated mercury salts, $HgX_2.2NH_3$,[6] and amido mercuric compounds, NH_2HgX,[6] leaving the so-called salts of Millon's base and related compounds to be formulated in accordance with the theory that they are substituted ammonium salts.

4. The Author's Theory.—The theory of the writer concerning the nature of the mercury ammonia compounds may be very simply stated as follows: All mercury ammonia salts are members of three general classes of compounds; they are either (1) normal mercuric salts with ammonia of crystallization, (2) ammonobasic mercuric salts, or (3) mixed aquobasic

[1] Handb. anorg. Chem. (Gmelin-Kraut), **3**, 818–840 (1875). Dict. Chem. (Watts), **3**, 206 (1892). Handwörterb. Chem. (Ladenburg), **10**, 148 (1892).

[2] Ammonium chloride in which two ammonium hydrogen atoms are replaced by the group -Hg-O-Hg-.

[3] Ammonium chloride in which the divalent mercury atom is supposed to replace one hydrogen atom in each of two molecules of the salt.

[4] Ammonium chloride in which two atoms of hydrogen in each molecule are replaced by a divalent mercury atom.

[5] Handb. anorg. Chem. (Gmelin-Kraut), **3**, 818 (1875). Dict. Chem. (Watts), **3**, 206 (1892). Handwörterb. Chem. (Ladenburg), **10**, 148 (1892). Handb. anorg. Chem. (Abegg), **3**, II, 866 (1905). Hofmann and Marburg: Ann. Chem. (Liebig), **305**, 191 (1899). Fürth: Monatsh., **23**, 1147 (1902). Strömholm: Z. anorg. Chem., **57**, 72 (1908).

[6] X = Cl, Br, I, NO_3, $\frac{1}{2}SO_4$, etc.

ammonobasic mercuric salts. The mercury ammonia bases, that is, Millon's base and its dehydration and deammonation products, are mixed aquo ammono bases.[1]

Of the theories thus briefly outlined, it is the dimercuriammonium theory of Rammelsberg which has found the widest acceptance among the writers of handbooks and dictionaries of chemistry. This theory will therefore be taken up again and discussed in detail after a few pages devoted to the elaboration of the theory which the writer hopes to establish.

III. AMPLIFICATION OF THE AUTHOR'S THEORY

5. Mercuric Salts with Ammonia of Crystallization.—Among the most familiar phenomena in the whole field of chemistry is the existence of compounds, especially salts, containing water of crystallization. Quite as numerously recorded in the literature are the compounds formed by the direct union of ammonia with salts and other substances, which show properties that are strictly analogous to those exhibited by salts with water of crystallization. Such compounds are therefore properly designated as ammonated salts or as salts with ammonia of crystallization. As the nature of the union between water and salt is ordinarily ignored in writing the formulas for salts with water of crystallization, so for our purpose it will be sufficient to write the formulas of the compounds formed by the addition of ammonia to the salts of mercury as simple addition products, for example, $HgCl_2.2NH_3$, and $HgCl_2.12NH_3$, $HgI_2.2NH_3$, $3HgI_2.4NH_3$ and $Hg(NO_3)_2.2NH_3$, for mercuric chloride, mercuric iodide and mercuric nitrate with ammonia of crystallization. These compounds are formed by the action of ammonia, either in the gaseous or liquid state or in solution in water, on the salts of mercury, provided that in the latter case an appropriate ammonium

[1] The theory thus outlined is in accordance with the ideas held over sixty years ago by Kane [Ann. chim. phys., **72**, 337 (1839); Elements of Chemistry, American Edition, **1843**, pp. 500–504] concerning the constitution of the compounds under consideration; for he clearly pointed out the fact that the fusible white precipitate is one of a large number of compounds in which ammonia plays a part analogous to that of water in salts containing water of crystallization; he recognized that the infusible white precipitate is a compound related to ammonia as the ordinary basic salts are related to water; he also observed that the yellow salts, later known as the salts of Millon's base, are compounds resembling basic salts.

salt is in solution in sufficient concentration to prevent the ammonolysis of the mercury salt. As in aqua ammonia, so also in liquid ammonia solutions, mercuric salts undergo ammonolysis[1] unless such action is prevented by the presence of an ammonium salt in the solution. Mercury salts with ammonia of crystallization are generally obtained in the form of crystals which show a definite ammonia vapor tension. Those which lose ammonia with sufficient ease, $HgI_2.2NH_3$ and $HgCl_2.12NH_3$, for example, may readily be observed to exhibit the phenomenon of efflorescence when exposed to the air. Mercuric salts with both ammonia and water of crystallization are also known, a representative compound being that of the formula $HgSO_4.2NH_3.H_2O$.

6. *Ammonobasic Mercuric Salts.*—It happens that most ammono bases, ammono salts and ammonobasic salts —for example, potassium amide, magnesium acetamide, potassium ammonozincate, and the ammonobasic lead salts[2]— are completely hydrolyzed in the presence of water, from which it follows that such compounds in general can be formed only from liquid ammonia solutions, or in any event, only in the presence of solvents other than water. The compounds formed by the action of ammonia on mercuric salts and mercuric oxide, however, are conspicuous exceptions to this rule. They are capable of existence in the presence of water, which accounts for the fact that many ammonobasic mercuric compounds have been prepared in the past and are found described in the literature under various names, for the most part as mercuriammonium compounds. Examples of some of the simpler ammonobasic salts of mercury are the infusible white precipitate, NH_2-Hg-Cl, the analogous bromide and nitrate, NH_2-Hg-Br and NH_2-Hg-NO_3, and the ammonobasic bromides and iodide of the respective formulas Br-Hg-NH-Hg-Br, Hg:N-Hg-Br and Hg:N-Hg-I.[3]

[1] Cf. THIS JOURNAL, **47**, 312 (1912).

[2] J. Am. Chem. Soc., **27**, 842 (1905).

[3] In accordance with the Rammelsberg-Pesci theory these compounds are given respectively the formulas $Hg_2NCl.NH_4Cl$, $Hg_2NBr.NH_4Br$, $Hg_2NNO_3.NH_4NO_3$, $Hg_2NBr.HBr$, Hg_2NBr and Hg_2NI, the first three thus being represented as double salts of dimercuriammonium and ammonium, the fourth as a compound of dimercuriammonium bromide and hydrobromic acid, and the fifth and sixth as simple dimercuriammonium salts.

7. *Mixed Aquobasic Ammonobasic Mercuric Salts.*—In addition to their ammonolytic tendency, mercuric salts, generally speaking, are also susceptible to hydrolysis. The halogen salts, excepting the fluoride, and certain ammono salts, such as mercuric acetamide, for example, are but slightly hydrolyzed, while the oxygen salts are highly hydrolyzed in aqueous solutions. In aqua ammonia solutions, then, or in contact with mixtures of ammonia and water,[1] mercuric salts may be expected to undergo both ammonolysis and hydrolysis, either simultaneously or successively, with the formation of products which are basic at the same time to both ammonia and water.

As NH_2-Hg-Br is the formula for the simplest ammonolytic decomposition product of mercuric bromide, so HO-Hg-Br is the formula for the analogous aquobasic salt, which, however, is not known to exist. And just as the considerable number of known aquobasic mercuric bromides may be formulated as derived from the hypothetical basic bromide, HO-Hg-Br, by dehydration and further hydrolysis, so, analogously, the ammonolysis and deammonation of mercuric bromide is known to yield the following ammonobasic products, namely, NH_2-Hg-Br, Br-Hg-NH-Hg-Br, $Hg_9N_4Br_6$ and Hg:N-Hg-Br, in accordance with the equations given on pages 371 to 372. Now, since mercuric salts, in the presence of aqua ammonia, undergo both ammonolysis and hydrolysis, either successively or simultaneously, and since the resulting basic products may further lose either water or ammonia or both water and ammonia, it follows that the theory accounts for a considerable variety of mixed basic salts.

However, just as it is impossible to assign constitutional formulas to the ordinary basic salts, especially the more complex among them, so it is futile to attempt the structural formulation of these mixed basic mercury salts. The best known mixed basic salt, chloride of Millon's base, for example, may be given the formula Hg:N-Hg-Cl.H_2O, or HO-Hg-NH-Hg-Cl, or NH_2-Hg-O-Hg-Cl, or NH_2-Hg-Cl.HgO, or any

[1] Cf. Franklin: J. Am. Chem. Soc., **29**, 55 (1907).

one of a dozen or more possible formulas representing the salt as a mixed basic compound.

IV. THE AMMONOLYSIS AND HYDROLYSIS OF MERCURIC SALTS

Disposing of all the earlier investigations upon the mercury ammonia compounds with the general statement that no experimental facts are on record which are entirely incompatible with the theory defended in this paper, we may now proceed to show that the theory receives convincing support from the recent work of the writer, François, Strömholm, Widman and Gaudechon, to which reference has already been made.

8. Mercuric Chloride.—As has already been stated, the fusible white precipitate is formed by the direct addition of ammonia to mercuric chloride when the latter is treated with liquid ammonia. In the presence of an excess of the liquid an addition product is formed having the composition $HgCl_2 \cdot 12NH_3$, and at the same time ammonolysis takes place, resulting in the conversion of a small portion of the salt into the infusible white precipitate, the quantity of which may be increased at pleasure by the addition of an alkaline amide, sodium amide for example. Inversely, the infusible white precipitate, an ammonobasic salt, is converted into the normal salt by the action of a sufficiently concentrated liquid ammonia solution of ammonium chloride. This reaction—taking place, it is to be remembered, in liquid ammonia— which is represented by the reversible equation

$$1.\quad HgCl_2 + 2NH_3 \rightleftharpoons NH_2\text{-}Hg\text{-}Cl + NH_4Cl$$

is strictly analogous to the action of water on hydrolyzable salts, and the inverse action of hydrochloric acid on the products of hydrolysis, as has been shown in detail in a preceding paper.[1]

Entirely similar changes take place when mercuric chloride is treated with aqueous ammonia, excepting that under these conditions the hydrolytic action of the water superimposes itself upon the ammonolytic action of the ammonia when the

[1] THIS JOURNAL, 47, 312 (1912).

concentration of the ammonium chloride is made sufficiently low, with the result that the chloride of Millon's base, a mixed aquobasic ammonobasic salt, is formed.[1] Various investigators have observed that the fusible white precipitate, in contact with water, is stable only in the presence of a considerable concentration of ammonium chloride, and that when it is washed with water it is converted first into the infusible white precipitate, and finally, after long washing, into the chloride of Millon's base. Contrariwise, by digestion with ammonium chloride solution of appropriate concentration, the latter compound is changed first into the infusible white precipitate and then into the fusible white precipitate.

The action of water on the white precipitates and the inverse action of ammonium chloride solution[2] on the oxide of mercury, the chloride of Millon's base and the infusible white precipitate, which are represented by the reversible equations

2. $HgCl_2.2NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}Cl + NH_4Cl$
3. $2NH_2\text{-}Hg\text{-}Cl + H_2O \rightleftarrows HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl$[3] $+ NH_4Cl$
4. $HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + H_2O \rightleftarrows 2HgO + NH_4Cl$

are therefore again phenomena which are very similar to the formation of ordinary basic salts by the action of water on normal salts and the reconversion of the former into the latter by an excess of acid. Equation 2 represents an ammonolytic reaction, Equations 3 and 4 represent hydrolytic reactions accompanied by simultaneous elimination of ammonia.

The writer began a study of the above equations in accordance with the principles of the Phase Rule, as suggested for the identification of ordinary basic salts by Miller and Kenrick[4] and applied by Allen[5] and by Cox,[6] but the work was

[1] *Vide infra* Equation 3.

[2] The fact is again emphasized that ammonium salts in solution in liquid ammonia exhibit many of the characteristic properties of acids. Even in water solutions their acid properties are frequently in evidence, as has been pointed out in an earlier paper [THIS JOURNAL, **47**, 287 (1912).]

[3] Or $NH_2Hg\text{-}O\text{-}Hg\text{-}Cl$, or $Hg_2NCl.H_2O$, or $NH_2HgCl.HgO$, etc.

[4] J. Physic. Chem., **7**, 259 (1903).

[5] THIS JOURNAL, **25**, 307 (1900).

[6] Z. anorg. Chem., **40**, 146 (1904).

interrupted by the San Francisco earthquake before much progress had been made.[1]

In the meantime, Strömholm and Gaudechon have independently determined the equilibrium concentration of ammonium chloride for Equations 2 and 3, both in water and aqueous ammonia, and have also proved Equation 4 to be reversible, without, however, determining the concentration of ammonium chloride in equilibrium with mercuric oxide and the basic salt HO-Hg-NH-Hg-Cl.

In the presence of insufficient ammonia for the realization of the above indicated reactions—that is, in the presence of an excess of mercuric chloride—Strömholm found the reactions represented by the equations

5. $HgCl_2.2NH_3 + HgCl_2 \rightleftarrows NH_2\text{-}Hg\text{-}Cl.HgCl_2 + NH_4Cl$

6. $4(NH_2\text{-}Hg\text{-}Cl.HgCl_2) \rightleftarrows (Hg:N\text{-}Hg\text{-}Cl)_2.HgCl_2$[2] $+ 2NH_4Cl + 3HgCl_2$

7. $Hg_5N_2Cl_4 + 4H_2O \rightleftarrows 4HgO + HgCl_2 + 2NH_4Cl$

to take place.

Strömholm was not sure of the existence of a chemical individual of the formula $Hg_5N_2Cl_4$. Gaudechon, on the contrary, obtained results pointing sharply to the formation of this compound, and asserted his belief that no compounds intermediate in composition between $Hg_5N_2Cl_4$ and the normal salt exist; that is, Gaudechon does not accept the existence of a compound of the formula $NH_2HgCl.HgCl_2$. However all this may be, the point of most significance in the present connection is that, whether compounds or mixtures, these substances are ammonobasic products formed by the progressive ammonolysis and hydrolysis of mercuric chloride, and which, in the presence of ammonium chloride in sufficient concentration, are reconverted into the normal salt.

In view of the showing thus made by Strömholm and Gaudechon that the solid phases, $HgCl_2.2NH_3$, NH_2HgCl, $HgCl_2.NH_2HgCl$, $(Hg_2NCl)_2.HgCl_2$, $Hg_2NCl.H_2O$ and HgO, only, are capable of existence in a system made up of the constituents

[1] J. Am. Chem. Soc., **29**, 40 (1907).

[2] $(Hg_2NCl)_2.HgCl_2 = Hg_5N_2Cl_4$.

mercury chloride, ammonia and water, it follows that the considerable number of other products which have been prepared in the past by the action of solutions of ammonia on mercuric chloride must be stricken from the list of chemical individuals. These products must have been basic mixtures in which, in particular instances, the constituent compounds happened to approximate molecular ratios.[1]

9. *Mercuric Bromide.*—In their investigations upon reactions in liquid ammonia Franklin[2] and Fitzgerald[3] have shown that mercuric bromide, when brought into contact with liquid ammonia, dissolves readily and at the same time undergoes ammonolysis in accordance with the reversible equation

8. $2HgBr_2 + 4NH_3 \rightleftarrows Hg{:}N\text{-}Hg\text{-}Br + 3NH_4Br$

Widman has studied the action of aqua ammonia in excess on mercuric bromide and has demonstrated the ammonolytic and hydrolytic reactions represented by the equations

9. $HgBr.2NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}Br + NH_4Br$

10. $2NH_2\text{-}Hg\text{-}Br \rightleftarrows Hg{:}N\text{-}Hg\text{-}Br + NH_4Br$

11. $Hg{:}N\text{-}Hg\text{-}Br + H_2O \rightleftarrows 2HgO + NH_4Br$

establishing their reversibility and determining the equilibrium concentration of the ammonium bromide, with accuracy in the case of Equations 9 and 10 and with rough approximation only in the case of Equation 11. Accurate measurements of the concentration of the ammonium bromide in equilibrium with the compound Hg_2NBr and mercuric oxide could not be accomplished because of the extreme slowness with which the equilibrium establishes itself and the very low concentration of the ammonium bromide in solution.

The above equations are realized only in the presence of an excess of ammonia, and from them it is seen that the decompositions of mercuric chloride and mercuric bromide follow the same course excepting that mercuric chloride forms a mixed ammonobasic aquobasic salt as shown in Equation 3, whereas, in the case of mercuric bromide, the hydrolytic

[1] Cf. J. Am. Chem. Soc., **29**, 51 (1907).
[2] *Ibid.*, **27**, 839 (1905).
[3] *Ibid.*, **29**, 656 (1907).

action of the solvent does not show itself until the final action represented in Equation 11 sets in.

In contact with pure water, both Widman and Gaudechon have shown the decomposition of the compound $HgBr_2.2NH_3$ to take place in accordance with the equations

12. $HgBr_2.2NH_3 \rightleftharpoons NH_2\text{-}Hg\text{-}Br + NH_4Br$

13. $9NH_2\text{-}Hg\text{-}Br \rightleftharpoons (Hg{:}N\text{-}Hg\text{-}Br)_4.HgBr_2 + 3NH_4Br + 2NH_3$

The further action of water on the ammonobasic salt $Hg_9N_4Br_6$ has not been determined, but Widman has shown that ammonium bromide solution, in the absence of free ammonia, acts upon mercuric oxide in the manner represented by the equation

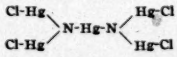
14. $9HgO + 6NH_4Br \rightleftharpoons (Hg{:}N\text{-}Hg\text{-}Br)_4.HgBr_2 + 2NH_3 + 9H_2O$

Equation 12 represents an ammonolytic reaction which is identical with that represented by Equation 9. Equation 13 shows that the compound $Hg_9N_4Br_6$[1] is formed by the simultaneous ammonolysis and deammonation of the ammonobasic salt NH_2HgBr.

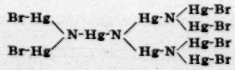
In the presence of an excess of mercuric bromide, Widman has established the following reactions:

[1] Gaudechon (*loc. cit.*) explains the formation of the compounds $(Hg_2NCl)_2.HgCl_2$ and $(Hg_2NBr)_4.HgBr_2$ on the assumption that the halogen salts of dimercuriammonium, when given the choice of water, ammonium halide or mercuric halide, unite by preference with the latter to form complex salts which he calls the chloromercurate and bromomercurate of dimercuriammonium, respectively.

Interpreted in accordance with the theory of the writer, these products are ammonobasic salts or mixtures formed in the presence of insufficient ammonia to give the basic compounds richer in nitrogen, as already discussed. As an ammonobasic salt the one compound may be given the formula



and the other the formula



Of course, the presentation of these formulas and the others given elsewhere in this article is carrying the constitutional formulation of these salts much too far. The only justification of the space given them is to show that the structural formulation sometimes applied to the ordinary basic salts, and occasionally there carried to undue extremes, is also applicable to these basic compounds.

15. $HgBr_2.2NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}Br + NH_4Br$
16. $2NH_2\text{-}Hg\text{-}Br \rightleftarrows NH:(Hg\text{-}Br)_2 + NH_3$
17. $2NH:(Hg\text{-}Br)_2 + 3H_2O \rightleftarrows 3HgO + 2NH_4Br + HgBr_2$

and has also shown that in contact with aqua ammonia of sufficient concentration the ammonobasic salt $NH(HgBr)_2$ is successively ammonolyzed at first into $Hg_9N_4Br_6$ and then into Hg_2NBr, in accordance with the equations

18. $9NH:(Hg\text{-}Br)_2.5NH_3 = 2Hg_9N_4Br_6 + 6NH_4Br$
19. $2Hg_9N_4Br_6 + 4NH_3 = 9Hg:N\text{-}Hg\text{-}Br + 3NH_4Br$

10. Mercuric Iodide.—When under sufficient pressure, ammonia gas unites readily with mercuric iodide to form a pure white addition product of the composition represented by the formula $HgI_2.2NH_3$, which, when exposed to the air, rapidly loses its ammonia of crystallization, the red color of the "anammonous" salt reappearing as the ammonia escapes.

Mercuric iodide dissolves abundantly in liquid ammonia and at the same time undergoes ammonolysis with the formation of an ammonobasic salt in accordance with the equation[1]

20. $2HgI_2 + 4NH_3 \rightleftarrows Hg:N\text{-}Hg\text{-}I + 3NH_4I$

The ammonolytic behavior of mercuric iodide toward aqua ammonia has been shown by François[2] to be in accordance with the reversible equations

21. $HgI_2.2NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}I + NH_4I$
22. $2NH_2HgI \rightleftarrows Hg:N\text{-}Hg\text{-}I + NH_4I$

François has found that the reactions represented by these equations take place only when the compound $HgI_2.2NH_3$ is treated with aqua ammonia of very considerable concentration. In contact with dilute ammonia an ammonobasic salt of the formula $Hg_9N_4I_6$[3] is formed, while in the presence of an abundance of pure water mercuric iodide with ammonia of crystallization dissociates into mercuric iodide and ammonia.

[1] Franklin: J. Am. Chem. Soc., **27**, 838 (1905).
[2] *Loc. cit.*
[3] Obviously the iodine analogue of the compound obtained by Widman and Gaudechon (cf. Equation 12).

11. Aquo Mercuric Salts.—The oxygen or aquo mercuric salts are much more readily hydrolyzed than are the halogen salts, and as a consequence the ammonobasic aquobasic salts described in the literature, and which have been made by the action of aqua ammonia on aquo salts, are generally much more basic and of more indefinite composition than are the products obtained from the halogen salts.

The only aquo mercuric salt, to the investigation of whose behavior towards aqua ammonia the principles of the Phase Rule have been applied, is mercuric nitrate. Strömholm[1] has prepared the three compounds represented by the formulas $Hg(NO_3)_2.2NH_3$, NH_2HgNO_3 and Hg_2NNO_3, and has failed to find any evidence for the existence of the considerable number of other products of the action of ammonia on mercuric nitrate which are found recorded in the literature.[2] The compound $Hg(NO_3)_2.2NH_3$ is formed when mercuric nitrate is treated with aqua ammonia containing 30 per cent. or more of ammonium nitrate; when the concentration of ammonium nitrate is around 7 to 14 per cent., the ammonobasic salt NH_2HgNO_3 is formed; while the ammonobasic nitrate, $Hg_2N.NO_3$, is formed when the ammonium nitrate concentration is still lower. Although Strömholm was not able to establish equilibrium concentrations in these experiments as definitely as has been done for the halogen salts of mercury, there can nevertheless be scarcely any doubt that the equations

23. $Hg(NO_3)_2.2NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}NO_3 + NH_4NO_3$
24. $2NH_2\text{-}Hg\text{-}NO_3 \rightleftarrows Hg{:}N\text{-}Hg\text{-}NO_3 + NH_4NO_3$
25. $Hg{:}N\text{-}Hg\text{-}NO_3 + 2H_2O \rightleftarrows 2HgO + NH_4NO_3$

represent the successive ammonolysis and hydrolysis of mercuric nitrate in the presence of an excess of aqua ammonia.

V. THE RAMMELSBERG-PESCI DIMERCURIAMMONIUM THEORY

It has been shown in the above pages that many facts, including those brought to light in the most recent investigations, are in entire harmony with the theory of the writer.

[1] *Loc. cit.*
[2] Cf. J. Am. Chem. Soc., **29**, 59 (1907).

However, before the theory can be looked upon as established, it is desirable to reconsider the arguments upon which the dimercuriammonium theory of Rammelsberg-Pesci, the most widely accepted of the ammonium theories, is based.

12. Statement of the Theory.—Hofmann, in the course of his brilliant work on the substituted ammonias, observed[1] that it is possible to formulate the mercury ammonia compounds as ammonium salts and bases in which the ammonium hydrogen is replaced by mercury.

With but little more evidence in support of Hofmann's ideas beyond the fact that it is possible so to formulate the mercury ammonia compounds, the theory was accepted by Rammelsberg,[2] who proceeded to give it the form which, especially on the authority of Pesci,[3] has found its way into many of the dictionaries and handbooks of chemistry.[4]

As has already been stated,[5] it is assumed, in accordance with the Rammelsberg–Pesci dimercuriammonium theory, that all the mercury ammonia compounds are derivatives of the dimercuriammonium radical, Hg_2N-, that is, of ammonium in which the four hydrogen atoms are replaced by two atoms of mercury. Consequently such compounds as the aquo ammono base Hg:N-Hg-OH[6] and the ammono basic bromide Hg:N-Hg-Br are given the formulas Hg_2NOH and Hg_2NBr, thus representing them as the hydroxide and bromide of dimercuriammonium, respectively. Pesci assumes that the salts of dimercuriammonium are especially prone to the formation of hydrates and to union with ammonium salts and mercuric salts to form double salts and other complex addition products. He therefore gives the well known fusible white precipitate the formula $Hg_2NCl.3NH_4Cl$, the infusible precipitate the formula $Hg_2NCl.NH_4Cl$, the chloride of Millon's base the formula $Hg_2.NCl.H_2O$, and ammonia tur-

[1] Jahresb., **1856**, 408.

[2] J. prakt. Chem., [2] **38**, 588 (1888).

[3] Gazz. chim. ital., **19**, 509 (1889); **20**, 485 (1890). Z. anorg. Chem., **21**, 361 (1899).

[4] Handb. anorg. Chem. (Dammer), **2**, II, 896 (1894). Traité de chimie minérale (Moissan), **5**, 401 (1906). Dict. Chem. (Watts), **3**, 344 (1907). Handwörterb. Chem. (Fehling), **5**, 1091 (1890).

[5] Page 363.

[6] *Vide infra*, page 388.

pith, or sulphate of Millon's base, the formula $(Hg_2N)_2SO_4.H_2O$, to illustrate by a few of the best known compounds. Millon's base itself is assumed to be hydrated dimercuriammonium hydroxide and in consequence receives the formula $Hg_2NOH.xH_2O$.

Pesci and his followers have been so thoroughly convinced that the dimercuriammonium radical is a never-failing constituent of all mercury ammonia compounds that they have been led to absurd extremes in their attempts to formulate some of these products; as, for example, when Pesci[1] gives the simple compound $HgCl_2.NH_3$ the formula $Hg_2NCl.3NH_4Cl.2HgCl_2$, and to what must have been a partially ammonolyzed specimen of ammonated mercuric iodide, $9HgI_2.10NH_3.NH_2HgI$, the formula $3NHg_2I.8NH_4I.4HgI_2$; or when Balestra[2] is led to formulate the ammonobasic compounds $NH(HgCl)_2$ and $HgCl_2.NH_2HgCl$ as $Hg_2NCl.HCl$ and $Hg_2NCl.2HCl$, respectively; or, perhaps as the climax of all, when Rây[3] is led to formulate the double salt $2HgCl_2.NH_4Cl$ as a compound of dimercuriammonium chloride with four molecules of hydrochloric acid, as represented by the formula $Hg_2NCl.4HCl$. For further examples of this method of formulating products of this kind, certain of which must be basic mixtures and not chemical individuals, the reader is referred to the papers by Pesci and his students.[4]

13. Refutation of the Theory.—As stated above, the dimercuriammonium theory has been accepted and developed upon what seems to the writer to have been entirely inadequate experimental evidence. Outside of the purely formal possibility of writing the mercury ammonia compounds as derivatives of dimercuriammonium, practically the only arguments which have been advanced in favor of the Rammelsberg-Pesci theory are: (1) those based on the properties of Millon's base; (2) those based on the action of water on the fusible and infusible white precipitates; (3) those concerning the behavior of the white precipitates toward solutions of potassium

[1] Italian Dictionary.

[2] J. Chem. Soc., **62**, 276 (1892).

[3] P. Chem. Soc. **17**, 96 (1901). Traité de chimie minérale (Moissan), **5**, 404 (1906).

[4] Z. anorg. Chem., **18**, 208 (1897); **21**, 376 (1899). Gazz. chim. ital., *loc. cit.*

hydroxide; (4) those based on the action of ammonium halides on various mercury ammonia compounds; (5) the arguments of Gaudechon based on the formation of certain so-called hydrated and ammonated dimercuriammonium salts ("chlorures et bromures de dimercuriammonium ammoniacaux"); (6) those based upon the results of the application of the methods of thermochemistry to the elucidation of the nature of the mercury ammonia compounds. A brief statement of these arguments, together with an attempt at their refutation, will be followed (7) by a repetition of Hofmann and Marburg's arguments against the validity of the Rammelsberg-Pesci theory, based on the existence of amine analogues of the white precipitates and the chloride of Millon's base.

(1) The compound $2HgO.NH_3.nH_2O$, known as Millon's base, and formed by the action of ammonia on mercuric oxide, shows marked basic properties. It absorbs carbon dioxide with avidity, and when brought into contact with solutions of such salts as potassium nitrate or sodium chloride it appropriates the anion of the salts to form insoluble salts of Millon's base, leaving the hydroxide of the alkali metal in solution. Even barium sulphate, according to Gerresheim,[1] is decomposed in a similar manner. In consideration of this behavior the strength of Millon's base has been assumed to be even greater than that of the alkali hydroxides, and this, in view of the weak basic properties of both mercuric oxide and ammonium hydroxide, has led to the formulation of Millon's base as the hydrated hydroxide of dimercuriammonium, $Hg_2N.OH.nH_2O$. As the tetra-alkyl ammonium hydroxides are strong bases, so, it has been argued, are the supposed strong basic properties of Millon's base explained by giving it the formula of a quaternary mercuriammonium hydroxide. The assumption that Millon's base possesses very strong basic properties has recently received support from the thermochemical measurements of Gaudechon who finds that the heat evolution accompanying the action of hydrochloric acid and hydrobromic acid on Millon's base is of the order of that set free by the neutralization of the strongest bases.

[1] Ann. Chem. (Liebig), **198**, 373 (1879).

Now the following considerations are advanced to show that it is not at all necessary to interpret the behavior of Millon's base as that of a conspicuously strong base. In the first place, its action on the soluble salts mentioned above certainly does not require such an interpretation. Even barium sulphate should be decomposed by a weak base provided that the sulphate of the base is less soluble than barium sulphate, and a weak base may form a stable carbonate when exposed to atmospheric air in the case that the solubility of the carbonate formed is sufficiently low. In the second place, while it must be admitted that Gaudechon's measurements of the amount of heat evolved by the action of the halogen acids on Millon's base constitute an argument of some force in favor of the hypothesis of strong basic properties of this base, the point is here made that other interpretations are not excluded, for it happens in some cases that the weaker acids and bases, on being neutralized, develop larger quantities of heat than characterizes the neutralization of the strongest acids and bases. In the third place, since salts formed by the action of strong acids on strong bases do not undergo hydrolysis to an appreciable extent, it follows, inasmuch as such a salt as the hydrated dimercuriammonium chloride undergoes hydrolysis in the presence of water,[1] that Millon's base cannot be a very powerful one. Finally, the properties of Millon's base and its salts, as highly insoluble, amorphous or, at best, microcrystalline substances, are in striking contrast with the ready solubility and the crystalline character of the alkylammonium bases and salts, to which Rammelsberg and Pesci assume them to be analogous, and, as a matter of fact, are just the properties which are in harmony with the theory that the base and its salts are mixed aquobasic ammonobasic compounds. Just as the ordinary aquobasic salts are generally insoluble and amorphous, so are the salts of Millon's base obtained as insoluble, amorphous precipitates.

While, therefore, in all probability not the powerful base it has been assumed to be, Millon's base may nevertheless possess basic properties considerably stronger than those shown by

[1] *Vide supra*, Equation 4, p. 369.

mercuric oxide without the necessity of assuming for it the constitution of a quaternary ammonium hydroxide. Although the analogy is rather remote, the fact that such compounds as CH_3HgOH, C_6H_5HgOH, $(CH_3)_3SnOH$ and other similar compounds of polyvalent metals containing but one hydroxyl group show strong basic properties may be taken as indicating that if Millon's base be formulated as mercuric hydroxide in which one of the hydroxyl groups is replaced as represented in the formula HO-Hg-NH-Hg-OH, then this formula may represent a compound distinctly more basic than mercuric oxide.

(2) From the fact that the fusible and infusible white precipitates readily undergo decomposition in contact with water, losing ammonium chloride and giving the compound represented by the formula $Hg_2NCl.H_2O$ as a final insoluble product, it has been argued that the two compounds named above are to be represented by the formulas $Hg_2NCl.3NH_4Cl$ and $Hg_2NCl.NH_4Cl$.

Now, in greater or less disagreement with these conclusions of Rammelsberg, the following arguments are advanced, some of which are to be found elsewhere in the literature. First, it has been shown above[1] that the stepwise decomposition of the fusible white precipitate by the action of water is much better explained as the result of ammonolysis of the normal mercuric chloride with ammonia of crystallization rather than on the assumption of the dissociation of a double salt into its simpler salt constituents. Second, in view of the fact that François[2] has prepared three compounds which may be represented by the three addition formulas $HgI_2.NH_3$, $3HgI_2.4NH_3$ and $HgI_2.2NH_3$, it certainly seems advisable to write these formulas as here given, at least until more knowledge has been gained of the nature of the compounds formed by the union of salts with water, alcohols, ammonia, the amines, etc., rather than to select the last one and give it the formula $Hg_2NI.3NH_4I$, as required by the theory of Rammelsberg, and assume the other two to be mixtures, as Pesci[3] has done

[1] Page 369.
[2] *Loc. cit.*
[3] Traité de chimie minérale (Moissan), **5**, 414 (1906).

for the compound $HgI_2.NH_3$, or to force them into the class of dimercuriammonium compounds and assign them complex, entirely improbable formulas. Third, the compound $HgI_2.2NH_3$ decomposes very readily[1] when exposed to the air or when placed in contact with water, into mercuric iodide and ammonia, in accordance with the equation[2]

$$HgI_2.2NH_3 \rightleftharpoons HgI_2 + 2NH_3$$

while in contact with aqueous ammonia the decomposition takes the now familiar form represented by the equation already given.[3] If the equation to which reference has been made points to the constitution represented by the formula $Hg_2NI.3NH_4I$ for François' compound, the above equation as conclusively proves its constitution to be that represented by the formula $HgI_2.2NH_3$, and there is no obvious reason why a double salt of the former formula should so easily give ammonia and mercuric iodide as products of decomposition.

(3) Rammelsberg[4] has interpreted the facts that the fusible and infusible white precipitates, in the presence of potassium hydroxide in excess, readily give off one-half and three-quarters of their nitrogen, respectively, in the form of ammonia in accordance with the equations

$$Hg_2NCl.NH_4Cl + KOH = Hg_2NCl.H_2O + KCl + NH_3$$

$$Hg_2NCl.3NH_4Cl + 3KOH = Hg_2NCl.H_2O + 3KCl + 3NH_3$$

as proving these compounds to be double salts of dimercuriammonium chloride and ammonium chloride; and Pesci[5] insisted on the validity of his interpretation of these reactions even after Hofmann and Marburg[6] had shown that the decomposition does not stop at the formation of the compound $Hg_2NCl.H_2O$, but that potassium hydroxide solutions at boiling temperatures decompose this substance, giving, as the final

[1] François: *Loc. cit.*

[2] Although much less readily, the fusible white precipitate and the bromine analogue apparently decompose in a similar manner.

[3] Page 373.

[4] *Loc. cit.*

[5] Z. anorg. Chem., **21**, 361 (1899).

[6] Ann. Chem. (Liebig), **305**, 194 (1899).

products of the action, mercuric oxide, potassium chloride and ammonia in accordance with the equation

$$Hg_2NCl.H_2O + KOH = 2HgO + NH_3 + KCl$$

The explanation of these reactions of Pesci and of Hofmann and Marburg, in terms of the author's theory, is as follows:

It has been shown that the fusible white precipitate undergoes successive decomposition in contact with water in a manner represented by the reversible equations given above,[1] from which it appears that by sufficiently prolonged washing with water mercuric oxide may be obtained as the final product of the successive ammonolysis and hydrolysis of the normal salt with ammonia of crystallization. When the fusible white precipitate, $HgCl_2.2NH_3$, is brought into contact with a solution of potassium hydroxide, ammonolysis and hydrolysis take place just as they do when the salt is in contact with pure water, excepting that in the former case the neutralization of the acid[2] by the potassium hydroxide present inhibits the reverse reactions indicated by the equations to which reference has been made. Under the conditions of Pesci's experiments, the evolution of ammonia comes practically to an end with the formation of the chloride of Millon's base because of the very low concentration of ammonium chloride required to limit Equation 4[3] and also because of the extreme slowness with which the highly insoluble, basic salt, $Hg_2NCl.H_2O$, undergoes hydrolysis. Hofmann and Marburg were able to complete the hydrolysis of this basic salt within a reasonable period of time by operating at high temperatures, the effect of which is to facilitate the hydrolysis and the removal of the resulting ammonia.

If the reactions of Pesci are accepted as proving the presence of the dimercuriammonium radical in the white precipitates, then the formation of the compound $Hg_2NCl.H_2O$ by the action of potassium hydroxide solutions on the double salt $2HgCl_2.NH_4Cl$ leads inevitably to the formula $Hg_2NCl.4HCl$ for the latter compound, and as a matter of fact P. C.

[1] Page 369.
[2] Again the fact is emphasized that ammonium salts may act as acids.
[3] Page 369.

Rây,[1] the discoverer of this double salt, and a warm adherent of the Rammelsberg-Pesci theory, at first actually assumed it to have the constitution represented by the latter formula, although later[2] he apparently changed his mind and regarded it as a double salt.

It therefore seems to be entirely obvious that, whereas on the one hand the decomposition of the basic salt, $Hg_2NCl.H_2O$, by solutions of potassium hydroxide at high temperatures cannot be accepted as positively disproving Pesci's theory of the nature of the white precipitates, neither, on the other hand, can Pesci's reactions be considered as furnishing any proof whatsoever of the presence of the compound Hg_2NCl as a constituent of these substances.

(4) Pesci, finding that the fusible and infusible white precipitates and the chloride of Millon's base give off ammonia[3] in the presence of an excess of ammonium chloride in accordance with the equations

$$Hg_2NCl.3NH_4Cl + xNH_4Cl = 2HgCl_2.xNH_4Cl + 4NH_3$$
$$Hg_2NCl.NH_4Cl + (x + 2)NH_4Cl = 2HgCl_2.xNH_4Cl + 4NH_3$$
$$Hg_2NCl.H_2O + (x + 3)NH_4Cl = 2HgCl_2.xNH_4Cl + 4NH_3 + H_2O$$

came to the conclusion that he here had in his hands a method for determining the nitrogen in the dimercuriammonium radical, this radical being decomposed by the action of an excess of ammonium chloride and contributing one-fourth of the ammonia evolved in the reaction. On the basis of his discovery he proceeded to demonstrate the presence of the dimercuriammonium radical in a large number of mercury ammonia compounds, and drew the general conclusion that the dimercuriammonium radical is present in all of them.

In an entirely similar manner, as Hofmann and Marburg have already pointed out, he might have shown the presence of the dimercuriammonium radical in mercuric oxide, for this oxide, in the presence of an excess of ammonium chloride, is converted into mercuric chloride with the evolution of two molecules of ammonia for each atom of mercury, as indicated in the equation

[1] P. Chem. Soc., **17**, 96 (1901).
[2] J. Chem. Soc., **81**, 648 (1902).
[3] Two molecules of ammonia for each atom of mercury present in the compound.

$$HgO + (x + 2)NH_4Cl = HgCl_2.xNH_4Cl + 2NH_3 + H_2O$$

The explanation of the conversion of these several basic compounds into the normal mercuric chloride by the action of ammonium chloride has already been given.[1] The one thing which Pesci's experiments demonstrate is that the fusible white precipitate and other mercuric salts with ammonia of crystallization lose this ammonia readily in the presence of an excess of an ammonium salt. They furnish no proof whatever of the presence of a dimercuriammonium radical.

(5) Gaudechon obtained three compounds represented by the formulas $Hg_2NCl.H_2O$, $(Hg_2NCl)_2.H_2O$ and $(Hg_2NCl)_4.H_2O$, respectively, by the action of water on the white precipitates; by the action of dilute hydrochloric acid on the base, $(Hg_2N)_2O.4H_2O$, obtained from the yellow oxide of mercury; and by the action of dilute hydrochloric acid on the base of the same composition obtained from the red oxide of mercury. He not only obtained analytical results pointing sharply to the above formulas, but he found it impossible to change the water content of any one of them. Gaudechon explains his results on the assumption that the three compounds are hydrates of dimercuriammonium chloride in different states of condensation. Starting from mercuric chloride in solution, he obtains a hydrate of the condensed or complex radical $(NHg_2Cl)_n$; starting from the yellow oxide of mercury, a hydrate of the radical $(NHg_2Cl)_{2n}$; and from the red oxide, a hydrate of the radical $(NHg_2Cl)_{4n}$.

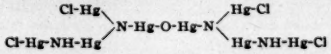
In accordance with the assumption that these compounds —if indeed they are really definite chemical compounds and not mixtures— are basic salts, they may be represented as successive dehydration products of the mixed ammonobasic aquobasic salt HO-Hg-NH-Hg-Cl,[2] and the inability of

[1] Page 368.

[2] Again carrying the constitutional formulation of these mixed basic salts beyond justifiable limits, the following equations are given to show just what is meant:

Cl-Hg-NH-Hg-OH + HO-Hg-NH-Hg-Cl = Cl-Hg-NH-Hg-O-Hg-NH-Hg-Cl

Cl-Hg-NH-Hg-O-Hg-NH-Hg-Cl + Cl-Hg-NH-Hg-O-Hg-NH-Hg-Cl =



Gaudechon to pass from one product to the other may find its explanation in the well known sluggishness with which dense, amorphous basic salts generally change their water content.

Gaudechon obtained the ammonated compounds $(Hg_2NCl)_2.NH_3$, $(Hg_2NCl)_4.NH_3$, $(Hg_2NBr)_2.NH_3$, $(Hg_2NBr)_4.NH_3$ and $(Hg_2NBr)_4.NH_3.H_2O$ by the action of ammonia upon certain of the above mentioned chlorides and upon the ammonobasic bromide of the formula Hg:N-Hg-Br, and found that they are reconverted into the original compounds by the action of water; that is, according to Gaudechon, the water of crystallization of the hydrated dimercuriammonium chloride, for example, is replaced by ammonia of crystallization in the presence of a large excess of ammonia, while ammonia of crystallization is replaced by water in the presence of an excess of this latter solvent. When the chloride of Millon's base is formulated as a basic salt, the reaction studied by Gaudechon may be explained as taking place in accordance with the equation

$$HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + H_2O$$

or

$$NH_2\text{-}Hg\text{-}O\text{-}Hg\text{-}Cl + NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + H_2O,$$

that is, whether or not the solid phase shall exist as an ammonobasic salt or a mixed basic salt depends upon the composition of the liquid phase.[1]

(6) Approaching the study of the mercury ammonia compounds from a new point of view, namely, by the application of the methods of thermochemistry, Gaudechon claims to have been able to elucidate the constitution of a considerable number of these compounds. In particular, he has measured the amounts of heat evolved in the reactions represented by the equations[2]

$$"(Hg_2NCl)_2.H_2O(\text{solid}) + 2NH_4Cl(\text{solid}) = 2Hg_2NCl.NH_4Cl(\text{solid}) + H_2O(\text{solid})"$$

and

$$"Hg_2NCl.NH_4Cl(\text{solid}) + 2NH_4Cl(\text{solid}) = Hg_2NCl.3NH_4Cl"$$

[1] It should be stated that Gaudechon found gaseous rather than liquid ammonia to act on the compound $Hg_2NCl.H_2O$.

[2] *Loc. cit.*, p. 188.

and finds that the quantity of heat set free, especially in the first equation, is of the order of that evolved in the reaction

$$\text{"}PtCl_4(solid) + 2KCl(solid) = K_2PtCl_6\text{"}$$

rather than that in the reaction

$$\text{"}CuCl_2(solid) + 2NH_4Cl(solid) = CuCl_2.2NH_4Cl\text{"}$$

and concludes that the compounds $HgCl_2.2NH_3$ and NH_2HgCl are not simple double salts, as represented above in accordance with the Rammelsberg-Pesci theory, but are complex salts to which, in another place,[1] he gives the formulas

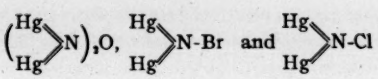
$$HCl\text{-}NHg_2\begin{matrix}Cl\\NH_3\end{matrix} \quad \text{and} \quad 3HCl\text{-}NHg_2\begin{matrix}Cl\\3NH_3\end{matrix}$$

respectively.

Such questionable formulas as these are avoided, and at the same time the thermochemical results find a much better explanation, on the assumption that the compound $Hg_2NCl.H_2O$ is a basic salt, which, when acted upon by an acid —ammonium chloride or hydrogen chloride associated with ammonia— forms first the less basic salt, NH_2HgCl, and finally the normal salt, $HgCl_2.2NH_3$. Just as the action between ordinary basic salts and acids is accompanied by large heat evolution, so also the conversion of ammonobasic salts into normal salts shows a heat change of similar order.

Gaudechon has also found[2] that the action of hydrobromic acid on Millon's base to form the compound Hg_2NBr is accompanied by the evolution of a larger quantity of heat than is set free by the action of hydrochloric acid on the same base. He compares these results with the well known fact that the conversion of mercuric oxide into mercuric bromide by the action of hydrobromic acid is a more strongly exothermic reaction than the corresponding formation of mercuric chloride by the interaction of mercuric oxide and hydrochloric acid, and remarks that, as the specific character of the mercury shows itself in these latter reactions, so it is retained in the mercury complexes

[1] *Loc. cit.*, p. 244.
[2] *Loc. cit.*, p. 236.



There is no obvious reason why this should be so on the basis of Gaudechon's method of formulating these compounds. If, however, Gaudechon's hydrated dimercuriammonium oxide be assumed to be a mixed aquo ammono base which, when acted upon by hydrochloric acid or hydrobromic acid, is converted into basic salts of the respective formulas HO-Hg-NH-Hg-Cl and Hg:N-Hg-Br, in which the halogen atom is represented as being in direct combination with the mercury, then the greater heat evolution accompanying the action of hydrobromic acid on the base, over and above that set free by the action of hydrochloric acid, finds an obvious and simple explanation.

It is plain, therefore, without considering the work of Gaudechon in further detail, that his thermochemical results constitute a strong element in support of the writer's view of the nature of the mercury ammonia compounds.

(7) Other and convincing arguments tending to show the inadequacy of the Rammelsberg-Pesci theory of the constitution of the white precipitates and the salts of Millon's base are based on the existence of certain mercury derivatives of the substituted ammonias. The amines and also certain acid amides react with the salts of mercury, though apparently not so readily as does ammonia itself, to form compounds which, until positive proof to the contrary is forthcoming, must be assumed to have the same constitution as the corresponding ammonia derivatives. The compounds $HgCl_2.2C_2H_5NH_2$, $HgI_2.C_6H_5NH_2$, $HgCl_2.2C_5H_5N$, $HgCl_2.2CON_2H_4$ and $HgCl_2.2CH_3CONH_2$, for example, are obviously the ethylamine, aniline, pyridine, urea and acetamide analogues, respectively, of the fusible white precipitate. It therefore necessarily follows, since these compounds cannot be formulated as derivatives of dimercuriammonium,[1] that the formula $Hg_2NCl.3NH_4Cl$ for the fusible white precipitate must

[1] To do so would necessitate the severance of a carbon nitrogen union, an action which could hardly be expected, and which, as a matter of fact, does not take place.

be erroneous. Hofmann and Marburg[1] have already presented this argument, but the fact that the supporters of the dimercuriammonium theory have either not answered it or have ignored it altogether,[2] has led to its repetition here.

Basing their arguments upon the supposed existence of an ethylamine analogue of the infusible white precipitate, C_2H_5NH-Hg-Cl, Hofmann and Marburg made out a similarly convincing case against the formula $Hg_2NCl.NH_4Cl$ for the infusible white precipitate. Since, however, Strömholm[3] has cast doubts on the existence of the ethylamine analogue of the infusible white precipitate, it may be pointed out that other analogues of the infusible white precipitate, such as C_6H_5NH-Hg-Cl[4] and CH_3NH-Hg-I,[5] have been prepared, the existence of which is incompatible with the dimercuriammonium theory.

We may bring this line of argument to a close by recalling Fürth's[6] preparation of the "chloride of a phenyl derivative

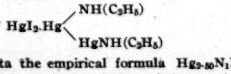
[1] Ann. Chem. (Liebig), **305**, 191 (1899).

[2] Pesci: Z. anorg. Chem., **21**, 361 (1899). Gaudechon: Ann. chim. phys., [8] **22**, 145 (1911).

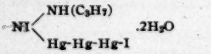
[3] Z. anorg. Chem., **57**, 72 (1908).

[4] Förster: Ann. Chem. (Liebig), **175**, 30 (1875).

[5] Charitschkoff: J. Russ. Physic. Chem. Soc., **39**, 230 (1907). In this paper by Charitschkoff are recorded some glaring examples of the manner in which insoluble mixtures sometimes find their way into chemical literature as definite compounds. By the action of Nessler's reagent upon a solution of methylamine, Charitschkoff obtained a yellow precipitate to which he ascribed the formula $Hg_2NI_2C_2H_{10}$, on the basis of analytical data leading to the formula $Hg_{2\cdot44}N_1I_{1\cdot87}C_{2\cdot48}H_{9\cdot61}$. Similarly, by the action of Nessler's reagent on ethylamine, he obtained a precipitate for which he gives the constitutional formula



while from his analytical data the empirical formula $Hg_{2\cdot80}N_1I_{1\cdot86}C_{4\cdot33}H_{11\cdot3}$ has been calculated. And worst of all, he finds the product of the reaction of Nessler's reagent on a solution of propylamine to yield, on analysis, the following results, expressed in percentages: Mercury, 69.6; iodine, 23.74; nitrogen, 2.20; carbon, 0.95; hydrogen, 0.41; oxygen (by difference), 3.10. These results lead to the formula $Hg_{4\cdot44}N_2I_{2\cdot98}C_1H_{5\cdot22}O_{2\cdot66}$, for his product, but he ascribes to it the empirical formula $Hg_4N_2I_2CO_2H_5$, and gives the following constitutional formula:



It may well be questioned whether it is desirable to encumber the pages of chemical literature with accounts of such work. The writer is under obligation to Dr. Elias Elvove, of the Division of Chemistry of the Hygienic Laboratory of the Public Health and Marine Hospital Service, for assistance in reading M. Charitschkoff's paper, which is in Russian.

[6] Monatsh., **23**, 1147 (1902).

of Millon's base," which compound obviously cannot be formulated as a dimercuriammonium derivative, but which readily lends itself to formulation as a mixed aquobasic anilinobasic salt,

$$C_6H_5NH\text{-}Hg\text{-}O\text{-}Hg\text{-}Cl^{1} \text{ or } HO\text{-}Hg\text{-}C_6H_5N\text{-}Hg\text{-}Cl$$

The existence of this compound must be accepted as a strong proof of the inadequacy of the Rammelsberg-Pesci formula for the chloride of Millon's base, to which it is obviously strictly analogous.

Finally attention is called to Strömholm's attempts to prepare potassium chloride double salts of formulas analogous to those given by Rammelsberg to the fusible and infusible, white precipitates.[2] Strömholm has rightly argued, since he was unable to prepare double salts of dimercuriammonium chloride and potassium chloride of the respective formulas $Hg_2NCl.3KCl$ and $Hg_2NCl.KCl$, that the ammonia compounds cannot properly be represented by the formulas $Hg_2NCl.3NH_4Cl$ and $Hg_2NCl.NH_4Cl$.

VI. THE MERCURY AMMONIA BASES

14. The Constitution of Millon's Base.—The amorphous, insoluble product of the action of aqua ammonia on mercuric oxide, generally known as Millon's base, has been assigned a bewildering number of formulas,[3] depending upon the view to be expressed concerning its empirical composition —for even this is uncertain— and its constitution. More recently, however, in accordance with the Rammelsberg-Pesci dimercuriammonium theory it has been assumed to be dimercuriammonium oxide or hydroxide, containing more or less water of crystallization, as indicated by the formulas $(Hg_2N)_2O.mH_2O$ and $Hg_2NOH.nH_2O$.

It is proposed to show here that Millon's base and its dehydration and deammonation products, instead of being derivatives of dimercuriammonium, are, as a matter of fact, mixed aquo ammono bases. Theoretically the simplest type of this

[1] According to Fürth.

[2] *Loc. cit.*, p. 91.

[3] Cf. Franklin: J. Am. Chem. Soc., **27**, 829 (1905); **29**, 40 and 45 (1907).

class of compounds, in its relation to the simplest water and ammonia bases, is represented by the second of the formulas

HO-Hg-OH	HO-Hg-NH_2	NH_2-Hg-NH_2
Aquo Base	**Mixed Aquo Ammono Base**	**Ammono Base**

No one of the bases presented by these formulas, however, is known to exist. Reactions which might be expected to result in the formation of mercuric hydroxide give instead its dehydration product, mercuric oxide. When potassium amide is allowed to act upon mercuric salts in solution in liquid ammonia,[1] mercuric nitride is obtained instead of either one of the theoretically possible ammono bases, mercuric amide or mercuric imide. Nor does a mixed base of the formula NH_2-Hg-OH exist, for Weyl[2] has shown that the action of dry ammonia on mercuric oxide results in the formation of the addition product $2HgO.NH_3$ instead of $HgO.NH_3$. The compound thus formed, however, may reasonably be interpreted as resulting from the deammonation of the simpler base in accordance with one of the equations

$$HO\text{-}Hg\text{-}NH_2 + H\,HN\text{-}Hg\text{-}OH = HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}OH + NH_3$$

$$HO\text{-}Hg\text{-}NH_2 + H\,O\text{-}Hg\text{-}NH_2 = HO\text{-}Hg\text{-}O\text{-}Hg\text{-}NH_2 + NH_3$$

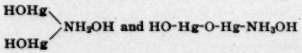
By the action of aqua ammonia on mercuric oxide a product is formed containing an additional molecule of water,[3] namely, Millon's base, or, as it is sometimes called, the hydrate of Millon's base. The compound is probably best represented by the simple addition formula $2HgO.NH_3.H_2O$ or $4HgO.2NH_3.H_2O$.[4]

[1] Franklin: J. Am. Chem. Soc., **27**, 835 (1905).

[2] Handb. Chem. (Gmelin-Kraut), 6te Aufl., **3**, 816 (1875).

[3] One-half molecule, according to Gaudechon.

[4] While a compound of the composition represented by the formula $2HgO.NH_3$ readily lends itself to constitutional formulation as a mixed base as has been done above, a compound containing a molecule (or one-half a molecule) of water cannot be so formulated. The formula for Millon's base, assuming it to have the composition represented by the first of the two empirical formulas given above, may be written HO-Hg-NH_2.HO-Hg-OH, HO-Hg-NH-Hg-OH.H_2O, or in a number of other ways representing it as a mixed basic compound; or it may be that the compound really is a substituted ammonium hydroxide as represented by one of the formulas



defended respectively by Hofmann and Marburg [Ann. Chem. (Liebig), **305**, 204 (1899)] and by Fürth [Monatsh., **23**, 1157 (1902)]. The point of view is emphasized here,

15. The Dehydration and Deammonation Products of Millon's Base.—The experimental results bearing upon the composition of the dehydration and deammonation products of Millon's base are in a rather chaotic state, as will be evident from a comparison of the recent results of Hofmann and Marburg,[1] on the one hand, with still more recent work of Gaudechon,[2] on the other.

Hofmann and Marburg obtained a product having approximately the composition represented by the formula Hg_3NHO_2,[3] by drying Millon's base in vacuo over sulphuric acid. Gaudechon found that under these conditions Millon's base loses both water and ammonia, but apparently made no effort to obtain a definite product as the result of this treatment of the base.

By drying Millon's base in an atmosphere of ammonia at laboratory temperature and 125°, Hofmann and Marburg obtained products represented by the formulas $2HgO.NH_3$[4] and Hg_2NHO,[5] respectively. In direct disagreement with the

however, that the basic properties of the compound are not due to ammonium hydroxyl but to hydroxyl in combination with mercury. In other words, that when hydrochloric acid, for example, acts on Millon's base to form its chloride, the action is to be represented by one of the equations

$$HO\text{-}Hg\text{-}(NH_2OH)\text{-}Hg\text{-}OH + HCl = HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + 2H_2O$$
$$HO\text{-}Hg\text{-}O\text{-}Hg\text{-}NH_2OH + HCl = NH_2\text{-}Hg\text{-}O\text{-}Hg\text{-}Cl + 2H_2O$$

and not by the equation of Hofmann and Marburg,

$$\begin{matrix} HOHg \\ \\ HOHg \end{matrix}\!\!>\!NH_2OH + HCl = O\!<\!\begin{matrix} Hg \\ \\ Hg \end{matrix}\!\!>\!NH_2Cl + 2H_2O$$

or others which are found in the literature representing the product formed as a substituted ammonium chloride.

[1] Ann. Chem. (Liebig), **305**, 21 (1899).

[2] Ann. chim. phys., [8] **22**, 148 (1911).

[3] As a mixed base this compound may be given either of the formulas 2HgO. HgNH or Hg: N-Hg-O-Hg-OH.

[4] Hofmann and Marburg have given this compound the formula $O\!<\!\begin{matrix} Hg \\ \\ Hg \end{matrix}\!\!>\!NH_2OH$; in accordance with the Rammelsberg-Pesci theory it receives the formula $\begin{matrix} Hg \\ \\ Hg \end{matrix}\!\!>\!N\text{-}OH$. H_2O; while the formulas Hg: N-Hg-OH.H_2O, HO-Hg-NH-Hg-OH, HgO.HgNH.H_2O or simply $2HgO.NH_3$ represent it as an aquo ammono base.

[5] According to Hofmann and Marburg, $O\!<\!\begin{matrix} Hg \\ \\ Hg \end{matrix}\!\!>\!NH$; according to the Rammelsberg-Pesci theory, $\begin{matrix} Hg \\ \\ Hg \end{matrix}\!\!>\!N\text{—}OH$; according to the writer, Hg: N-Hg-OH, or HgO.HgNH, or simply Hg_2NHO.

results of Hofmann and Marburg, Gaudechon obtained the compound Hg_2NHO by drying Millon's base in an atmosphere of ammonia at laboratory temperature, and the compound Hg_4N_2O[1] at 110°.

Hofmann and Marburg found that Millon's base is converted into mercuric oxide by the action of alcohol, and Gaudechon has shown that in contact with boiling water the base gives off ammonia until equilibrium is established at a certain low ammonia concentration, or, in case the ammonia is allowed to escape, until pure mercuric oxide is left behind. That is to say, the reversibility of the equation

$$2HgO + NH_3 + nH_2O \rightleftarrows 2HgO.NH_3.nH_2O$$

has been established.

Notwithstanding certain points of disagreement in the results obtained by these and earlier investigators[2] of the dehydration and deammonation of Millon's base, its general behavior stands out with sufficient clearness for present purposes. Heated in the presence of ammonia gas, the base loses water only to form the successive dehydration products of the empirical formulas $Hg_2NH_3O_2$, Hg_2NHO and Hg_4N_2O.[3] In vacuo over sulphuric acid, in contact with alcohol, or heated in contact with water, Millon's base loses both water and ammonia, giving in the latter two cases mercuric oxide as the final product. Now this is in a general way the behavior to be expected from a mixed aquo ammono base, for just as many hydroxides undergo dehydration, and certain metallic amides and imides similarly lose ammonia, so a mixed base, such as Millon's base is here assumed to be, might be expected to give up both water and ammonia, water only, or ammonia only, depending upon the composition of the vapor or liquid phase in contact with the compound. It also may be added finally that the very indefiniteness of composition

[1] According to Gaudechon, $\left(\begin{matrix}Hg\\ \diagdown\\ \quad N\\ \diagup\\ Hg\end{matrix}\right)_2O$; in accordance with the theory of the writer, Hg: N-Hg-O-Hg-N: Hg or $HgO.Hg_3N_2$.

[2] Cf. Franklin: J. Am. Chem. Soc., **29**, 45 (1907).

[3] Plantamour [Ann. Chem. (Liebig), **40**, 115 (1841)] and Hirzel [*Ibid.*, **84**, 258 (1852)] independently claimed to have obtained mercuric nitride by heating Millon's base in an atmosphere of ammonia.

strikingly shown by the investigations above quoted, together with the insolubility and generally amorphous character of Millon's base and its dehydration products, recall the very similar properties of many metallic hydroxides, thus adding further support to the writer's contention that Millon's base is a mixed aquo ammono base, and not a substituted ammonium hydroxide.

16. Action of Acids and Ammonium Salts on Millon's Base.[1]—When treated with dilute acids in limited quantity Millon's base is converted into what have been called the salts of Millon's base, or of dimercuriammonium. If excess of acid is used the action does not stop until the normal mercuric salt is formed. For example, assuming Millon's base to be a mixed water ammonia base, the action of hydrochloric acid is represented by the equations

$$HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}OH + HCl = HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + H_2O$$
$$HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + 4HCl = 2HgCl_2 + NH_4Cl + H_2O$$

Formulating the base as a hydrated dimercuriammonium hydroxide, the action is represented by the equations

$$Hg_2NOH.H_2O + HCl = Hg_2NCl.H_2O + H_2O$$
$$Hg_2NCl.H_2O + 4HCl = 2HgCl_2 + NH_4Cl + H_2O$$

The first equation represents the conversion of a base into a basic salt; the second of a basic salt into a normal salt. On the assumption that Millon's base is a hydrated dimercuriammonium hydroxide its conversion into a dimercuriammonium salt as represented in the third equation follows naturally enough, but there is no obvious reason why a quaternary ammonium radical should be destroyed by an excess of acid as represented in the fourth equation.

Millon's base is also converted into mixed basic salts by the action of dilute solutions of ammonium salts. For example, the action of ammonium chloride —which, as has already been explained, acts as an acid toward basic mercuric salts— on Millon's base is represented by the equation

[1] Hofmann and Marburg (*loc. cit.*) state that the dehydration product obtained by heating Millon's base to 125° in an atmosphere of ammonia is not attacked by dilute acids. This observation is in disagreement with the assumption that the compound is a mixed base and therefore requires confirmation.

$$HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}OH.nH_2O + NH_4Cl = HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}Cl + NH_3 + (n+1)H_2O$$

which is to be interpreted as representing the conversion of a mixed aquo ammono base into an aquobasic ammonobasic halogen salt of mercury by the action of the halogen acid, ammonium chloride. The further action of more concentrated solutions of ammonium chloride to form the ammonobasic halogen salt, NH_2HgCl, and the normal halogen salt with ammonia of crystallization, $HgCl_2.2NH_3$, has already been discussed.[1]

VII. MERCURY DERIVATIVES OF THE ACID AMIDES

17. Mercury Salts with Acid Amides of Crystallization.—A considerable number of metallic salts are known to unite directly with certain acid amides to form compounds in which the acid amide must be assumed to play a part similar to that exhibited by water, alcohol, ammonia and the amines in the compounds formed by direct union of these latter substances with salts. For example,[2] $HgCl_2.HCONH_2$ is the formula for mercuric chloride with formamide of crystallization; $CdCl_2.2CH_3CONH_2$, $HgI_2.2CH_3CONH_2$, $CuCl_2.2CH_3CONH_2$, $HgCl_2.CH_3CONH_2$, $NaBr.3CH_3CONH_2$ and $NaI.2CH_3CONH_2$, are formulas for salts with acetamide of crystallization; the formulas $Ca(NO_3)_2.6CON_2H_4$, $Mg(NO_3)_2.4CON_2H_4$, $ZnCl_2.2CON_2H_4$, and $HgCl_2.CON_2H_4$, represent salts with urea of crystallization.

Of these compounds it is the mercuric salts with acid amides of crystallization which are of particular interest in the present connection; for just as mercuric salts with ammonia of crystallization readily undergo ammonolysis to form ammonobasic salts, so the records in the literature show a number of reactions of the type represented by the equation

$$\begin{matrix} CH_2\text{—}CO \\ | \\ CH_2\text{—}CO \end{matrix}\!\!>\!NH + HgCl_2 = \begin{matrix} CH_2\text{—}CO \\ | \\ CH_2\text{—}CO \end{matrix}\!\!>\!N\text{-}Hg\text{-}Cl + HCl^3$$

which is seen to be strictly analogous to the ammonolytic

[1] Page 369.

[2] Handb. org. Chem. (Beilstein), **1**, 1237 and 1294 (1893).

[3] Ley and Schaefer: Z. physik. Chem., **42**, 696 (1903).

decomposition of mercuric salts as described in detail above.[1]

18. Ammono Mercuric Salts.—The writer has shown in an earlier paper[2] that those derivatives of the acid amides in which amide hydrogen is replaced by metal are the salts of an ammonia system of acids, bases and salts. The compounds represented by the formulas

$$CH_3CONHK, \quad (CH_3CONH)_2Zn \quad \text{and} \quad (CH_3CONH)_2Hg$$

are therefore ammonoacetates of potassium, zinc and mercury, respectively.

As has been pointed out elsewhere in this paper,[3] it happens that the mercury derivatives of the acid amides are stable in the presence of water, whereas most ammono salts of other metals are immediately hydrolyzed in the presence of this solvent. As a consequence of this peculiar stability of the ammono mercuric salts, many of them have been prepared in the past and are found described in the literature.

19. Amidobasic Mercuric Salts. Amidolysis.—Occupying an intermediate position between the ammono salts and the halogen salts a considerable number of compounds have been prepared, as, for example, $C_6H_5CONH\text{-}Hg\text{-}I$,[4]

N-Hg-Cl[5] and $HCON(C_6H_5)\text{-}Hg\text{-}Cl$,[6]

which are to be looked upon as mixed ammono halogen salts, that is, they are compounds partaking at the same time of the properties of ammono salts and halogen salts, just as the compounds $NO_3\text{-}Hg\text{-}I$[7] and $NO_3\text{-}Hg\text{-}Br$[8] may be considered to be mixed aquo halogen salts. It is also entirely legitimate to look upon such mixed ammono halogen salts —especially such as are derivatives of the weakest ammono acids— as

[1] Page 368.

[2] This Journal, **47**, 302 (1912).

[3] Page 3..o.

[4] Tafel and Enoch: Ber. d. chem. Ges., **23**, 1554 (1890).

[5] Menschutkin: Ann. Chem. (Liebig), **162**, 172 (1872). Ley and Schaefer: Z. phys k. Chem., **42**, 696 (1903).

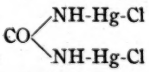
[6] Wheeler and McFarland: This Journal, **18**, 543 (1896).

[7] Or $HgI_2.Hg(NO_3)_2$. Preuss: Ann. Chem. (Liebig), **29**, 326 (1839). Kraut: Ber. d. chem. Ges., **18**, 3461 (1885).

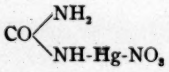
[8] Morse: Z. physik. Chem., **41**, 726 (1902).

amidobasic salts.[1] Accordingly, from this point of view, the benzamide mercuric iodide, mentioned above, is an amidobasic mercuric iodide and the succinimide mercuric chloride is an imidobasic mercuric chloride.

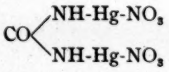
Another group of compounds which may be classed with amidobasic mercuric salts are certain of the well known mercury urea compounds.[2] For example,



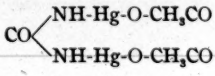
is an ureidobasic mercuric chloride;



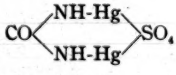
and



are ureidobasic mercuric nitrates;

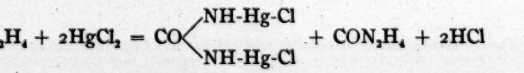


is an ureidobasic mercuric acetate, and



is an ureidobasic mercuric sulphate.

These compounds are related to urea as the infusible white precipitate and the analogous ammonobasic nitrate, acetate and sulphate are related to ammonia. Just as the infusible white precipitate is formed by the ammonolysis of mercuric chloride, so mercuric chloride in aqueous solutions reacts with urea in accordance with the equation



to form a ureidobasic mercuric chloride.

[1] Bruni and Manuelli [Z. Elektrochem., **11**, 554 (1905)] have called attention to the analogy between the action of water and that of formamide, respectively, upon chlorides of antimony and bismuth, and have given the name "amidolysis" to the action represented by the equations $SbCl_3 + 2HCONH_2 = (HCONH)_2SbCl + 2HCl$ and $SbCl_3 + 3HCONH_2 = (HCONH)_3Sb + 3HCl$.

[2] Handb. org. Chem. (Beilstein), 3te Aufl., **1**, 1292 (1893).

The urea analogue of Millon's base is the well known compound[1] formed by the action of urea on mercuric oxide and to which either of the formulas

$$CON_2H_4.2HgO \text{ or } CO\begin{<}\begin{matrix}NH\text{-}Hg\text{-}OH\\ NH\text{-}Hg\text{-}OH\end{matrix}$$

may be given.

VIII. MERCURY DERIVATIVES OF OTHER NITROGEN COMPOUNDS

20. Hydrazine and Hydroxylamine.—Two other nitrogen compounds —hydrazine and hydroxylamine— unite with mercury salts as hydrazine[2] and hydroxylamine[3] of crystallization, respectively.

Hofmann and Marburg[4] have observed that under the action of water the chloride of mercury with hydrazine of crystallization undergoes a decomposition which is analogous to the hydrolytic and ammonolytic decomposition, as is shown by the equation

$$2HgCl_2.N_2H_4 = Cl\text{-}Hg\text{-}NH\text{-}NH\text{-}Hg\text{-}Cl + N_2H_4.2HCl$$

IX. CONCLUSIONS

In the preceding pages the attempt has been made to show that the prevailing ammonium theories as applied to the so-called mercuriammonium compounds are entirely inadequate

[1] This compound, as well as the formamide mercuric oxide of Fischer and Grützner [Arch. Pharm., **232**, 329 (1894)], from this point of view are mixed bases, that is, they are compounds basic at the same time to water and an acid amide. From another point of view they may be considered to be aquobasic ammono salts; and from yet another, they may be looked upon as formyl and urea derivatives, respectively, of the hypothetical mixed ammono base, $NH_2\text{-}Hg\text{-}OH$ (cf. p. 388).

Ruspaggiari, a student of Pesci, assumes [Gazz. chim. ital., **27**, I (1897)] in accordance with the Rammelsberg-Pesci theory that this base is the hydroxide of the divalent radical $CO\begin{<}\begin{matrix}Hg:NH\text{-}\\ Hg:NH\text{-}\end{matrix}$, and that all the various mercury urea compounds are salts of this radical, which he calls mercuriurea. To the compound above formulated as ureidobasic mercuric chloride, therefore, Ruspaggiari gives the formula $CO\begin{<}\begin{matrix}Hg:NH\text{-}Cl\\ Hg:NHC\text{-}l\end{matrix}$, and to the compound $HgCl_2.CON_2H_4$ —mercuric chloride with urea of crystallization— the formula $CO\begin{<}\begin{matrix}Hg:NH\text{-}Cl\\ Hg:NH\text{-}Cl\end{matrix} . CO\begin{<}\begin{matrix}NH_2\\ NH_2\end{matrix}.2HCl$.

[2] Curtius and Schräder: J. prakt. Chem., [2] **50**, 332 (1894). Franzen and von Mayer: Z. anorg. Chem., **60**, 247 (1908).

[3] Adams: THIS JOURNAL, **28**, 198 (1902).

[4] Ber. d. chem. Ges., **30**, 2019 (1897). Ann. Chem. (Liebig), **305**, 214 (1899).

to the purpose of explaining the nature of this large and more or less obscure group of substances.

Especially has the dimercuriammonium theory of Rammelsberg–Pesci —which has received sufficient favor to find its way into many of the dictionaries and handbooks of chemistry as a basis for the classification of the mercury nitrogen compounds— been considered at length and found devoid of any sufficient basis in experimental facts.

A theory in explanation of the nature of the mercury ammonia compounds has been developed in accordance with which all compounds of the type of the fusible white precipitate are assumed to be mercuric salts with ammonia of crystallization; all those of the type of the infusible white precipitate and Nessler's precipitate are shown to be ammonobasic mercuric salts; while the compounds of the type of the salts of Millon's base are to be looked upon as mixed aquobasic ammonobasic salts, that is to say, as salts which are basic at the same time to both water and ammonia.

An attempt has been made to show that Millon's base itself, instead of being a hydrated dimercuriammonium oxide or hydroxide, is, as a matter of fact, a mixed aquo ammono base, that is, that it is a compound showing the properties of both an aquo base and an ammono base.

It is believed that the arguments given in this paper in support of the author's point of view are sufficient to establish the theory, at least in its fundamental outlines.

CHEMICAL DIVISION
U. S. PUBLIC HEALTH AND
MARINE HOSPITAL SERVICE
WASHINGTON, December, 1911

THE OZONIZATION OF OXYGEN BY α-RAYS[1]

BY S. C. LIND

1. Introduction

It has been frequently observed that air, remaining in contact with a strong source of radioactivity, becomes ozonized

[1] The experiments described in this paper were carried out in the Institut für Radiumforschung in Vienna during the past summer and were reported to the Vienna Academy at its meeting of November 30, 1911.

to an extent such as to furnish a marked odor of ozone on opening the containing vessel. Direct contact of the radioactive substance with air is not necessary, however, for the production of ozone, as may be shown by closing completely the source of activity, while allowing the α-rays to emerge through a thick mica window. A continuous formation of ozone takes place outside the window, which ceases when the mica is made sufficiently thick to cut off the α-rays. The continuous formation of ozone is also particularly striking in the immediate neighborhood of thin-walled glass bulbs containing considerable quantities of radium emanation. The determination of the amount of ozone thus formed, in a given time from a given quantity of emanation, seemed to present a question of some interest, and the results of experiments on this subject will be found in the present paper.

The method of preparing very thin-walled glass bulbs will be fully described in Section 2, but it may be mentioned here that the ones employed were one to two mm. in diameter and so thin-walled that their absorption of α-rays was equivalent to that of only one to two cm. of air. It was found advantageous to use pure oxygen instead of air in most cases, and to work under the conditions required for the full utilization of the α-rays, as well as those necessary for the chemical determination of the rather inconveniently small quantities of ozone. The apparatus employed will be fully described in succeeding sections.

The experiments led to the interesting discovery that the total number of ozone molecules produced in a given time is of the same order of magnitude as the total number of ions formed, during the same time, by the α-rays in passing through the oxygen gas. This would suggest an ionic theory for the formation of ozone, which is reserved for a fuller consideration after the experimental data have been presented. It may be stated, briefly, that the hypothesis is that ozone is formed by the union of an oxygen molecule with a charged oxygen atom (ion), and that the ozone later loses its charge. Whether the proposed hypothesis is correct or not, it is, at least, very significant that the quantity of ozone formed is,

in some cases, almost exactly equal to, and in no case exceeds, the amount required by the ionic theory. But in some other cases the quantity falls as much as several-fold below the theoretical This latter can be readily explained on the assumption of the recombination of ions to form ordinary oxygen, leaving unsettled the question as to why this process does not seem to proceed uniformly under similar experimental conditions. But aside from all theory remains the striking equivalence of chemical and of ionic action, which indicates some close relation between the two, either through cause and effect or as accompanying effects of a common cause.

2. Method of Preparation of Small Glass Bulbs Penetrable to α-Rays

The ranges in air of the α-rays from Emanation, Radium A and Radium C are 7.06, 4.83 and 4.23 cm., respectively, and the corresponding thicknesses of glass which they can penetrate are between 0.04 and 0.02 mm. Glass bulbs or capillary tubes of this degree of thinness will not withstand atmospheric pressure, except when very small in volume; nor can they be blown before the blast lamp by the usual method. In their classic research upon the formation of helium from α-rays, Rutherford and Royds[1] were able to prepare capillary *tubes* thin enough to be penetrated by α-rays, but no specifications were given for their method of preparation. Hence it was necessary to work out a method anew, using as guiding principles that the thin glass surfaces to be blown must be protected from the direct heat of the blast lamp by working in a hard-glass tube heated on the exterior, and that in order to blow the glass at this reduced temperature more than ordinary pressure must be employed. For the present experiments, *round bulbs* are more suitable than *capillary tubes*, such as used by Rutherford and Royds. The construction of the first bulbs by this method was carried out in conjunction with Prof. Duane in the laboratory of Mme. Curie in Paris.

One begins by drawing out, in a weak blast flame, a piece

[1] Rutherford and Royds: Phil. Mag., **17**, 291 (1909).

of soft glass tubing, 6–8 mm. in diameter and as thin-walled as available, until a capillary is produced about 1 mm. in diameter and 0.1 mm. in wall thickness. In order to draw this capillary part yet thinner, a simple oven is constructed out of a piece of Jena combustion tubing (15–20 cm. long) and three pieces of asbestos board, two of which, placed vertically, are pierced by the Jena tube, and the third piece is arched over the whole to reflect the heat inward. The Jena tube, open at both ends, is then clamped near one end in a horizontal position and heated below with a Teclu burner. The soft tube whose capillary part is to be drawn thinner is closed at one end and attached at the other to a foot blast, and then, while being revolved slowly in the oven, is drawn out under a pressure just sufficient to prevent its dropping in too greatly. This furnishes a tapering capillary of extreme thinness which should be broken off at the thinnest part at which one can blow a bulb (usually at a diameter of about 0.1–0.2 mm.), and is sealed by barely touching the minute end into a small flame. This closed tip is then introduced into the hottest part of the oven and is put under the highest pressure obtainable with a foot blast. Under favorable conditions, a perfect bulb will be formed at the end, having a diameter of 1 to 2 mm. and a wall thickness of 0.005 to 0.01 mm., which is, nevertheless, capable of withstanding atmospheric pressure in either direction. Failure to obtain results may be due to any of the following causes: capillary part chosen too narrow or originally too thick-walled; the pressure or the heat insufficient; the original glass too hard. The small bulb is left attached through the capillary to a short piece of the 6–8 mm. tubing, which can be joined to a thick-walled piece before sealing onto the purification apparatus. In case it is desired to detach the bulb after emanation is introduced and to seal off the glass completely or to close it with any nonconducting material, such as sealing wax, it is necessary first to seal a piece of platinum wire through the heavy stem to conduct away static charges, which would otherwise accumulate and destroy the bulb by sparking through.

3. A Radio-Optical Method to Determine the Power of Absorption of Thin Glass Bulbs for α-Rays

(*a*) *A Rough Estimation to Test the Usefulness of Empty Bulbs.*—Before the introduction of emanation into a new bulb, it is desirable to gain some information as to its wall thickness and consequent absorption. Such a determination presents no difficulties if a convenient source of α-rays is at hand, as, for example, a bulb already containing emanation. The source of α-rays is placed at a distance of 4 to 5 cm. above a horizontal zinc-sulphide screen. If the empty bulb being examined be brought between the screen and the source of radiation, its shadow will be projected on the screen, because the α-rays emerging from the bulb containing the emanation will not be able to penetrate both walls of the empty bulb and the intervening air layer of 4 to 5 cm. But on bringing the two bulbs nearer the screen, at a certain distance a spot of light will appear in the center of the shadow of the bulb, indicating that the rays which strike the glass walls *normally* are now just able to penetrate the two walls and the diminished air space. From a knowledge of the "air range" of the α-rays, the distance of the active source from the screen when the light center first appears, and the "air equivalent" of the wall of the bulb containing the emanation, one can estimate the "air equivalent" of the two walls of the new bulb. In case the two walls of the new bulb are too thick to be penetrated, information of value may be obtained by introducing a few grains of zinc sulphide directly into the bulb being examined to ascertain if a single wall is penetrable and whether it appears uniformly thin on all sides. The determination of the air equivalent of a bulb already filled with emanation is capable of greater precision, as will be described in the following paragraph.

(*b*) *A More Exact Method for Bulbs Containing Emanation.*—On approaching a zinc sulphide screen with a thin-walled bulb containing emanation, the appearance of a spot of light due to the α-rays is quite sudden, owing to their uniform velocity, and is easily distinguishable from the weaker phosphorescence due to the β-rays, which sets in at a much greater

distance from the screen and at no point undergoes a sudden increase. The distance from the screen on the appearance of first light may be taken directly as the "air range" for α-rays of Radium C outside the bulb; and the difference between this and the total "air range" of 7.06 cm. is the "air equivalent" of the bulb. However, since some degree of personal equation enters into this observation, it is more accurate to proceed as follows: On approaching nearer to the screen, the spot of light broadens into a circle which increases in size as the source of radiation nears the screen. A straight line from the outer edge of the light circle to the source is always the "air range" of the α-rays of radium C which pass through the glass wall at right angles, and should remain constant if the glass wall is of the same thinness in all directions, which is evidenced by the perfect form of the light circle. This maximum air range can then be calculated at any distance from the simple geometrical relation, $R^2 = L^2 + D^2$, where R is the air range, L the distance from the screen, and D the diameter of the light circle. The degree of constancy of R can be seen from the following table of measurements made on bulb A, used in later experiments:

Table I

L (in cm.)	D (in cm.)	R (in cm.)
5.8	2.5	5.9
5.4	5.0	5.9
5.0	6.4	5.9
4.5	7.3	5.8
4.1	8.5	5.9
3.3	10.0	6.0
	Average,	5.9 ± 0.03 cm.

These measurements must, of course, be carried out in the dark, which renders scale reading difficult, since the phosphorescent illumination from the screen is hardly sufficient. This difficulty has been overcome as follows: By bringing the vertical scale on which the distance from the screen is being measured very near the bulb containing emanation, an image of the latter is reflected on the scale and can be read

directly, if it is sufficiently bright to render the divisions visible, or its position is marked and then read by momentarily switching on an electric lamp. The diminutive size of this image favors its accurate location, and since the image is on the scale itself, parallax errors are avoided. The measurement of the diameter of the light circle on the screen is more difficult and it was found most satisfactory to use a pair of metal-pointed dividers in locating the boundaries of the circle. By scratching gently on the screen with the metal points, phosphorescent sparking is produced which enables one to see when the points are correctly located on the circumference of the circle of light. The dividers are then transferred to a scale and the distance between the points read off by momentary illumination, as above. These measurements are quite satisfactory for tubes containing not less than twenty millicuries of emanation; with smaller quantities the luminescent effects become too indistinct.

4. Corrections of the Absorptive Power of the Glass Walls

On account of the small radiating surface of these minute bulbs, the geometrical relations, which are usually simplified by the employment of "canalization," need not be taken into account here. On the other hand, it is evident that the thickness of glass penetrated by a ray, emerging in a straight line through the wall of a hollow sphere, will depend on the four factors: wall thickness; radius of the sphere; angle of incidence; and the position within the sphere from which the ray emanates.

The wall thickness itself is calculated from the value of the air equivalent of the glass wall, as determined by the method just described in Section 3, assuming 1 cm. of air to be equivalent to 0.005 mm. of glass. The total diameter of the bulb, which does not need to be known with much accuracy, is measured directly, the tenths being estimated on a mm. scale. From a knowledge of these two factors, the path can be found for all different angles and positions, remembering that only one-third of the α-rays come from gaseous emanation and the other two-thirds from induced activity, situated as solid

on the inner wall of the bulb. Since the number of ions produced along the course of an α-ray is not constant but increases rapidly towards the end of the path in a way not reducible to mathematical formulation, integration methods cannot be used to determine an average "air range" outside the bulb, which might be used in finding the total ionization; but the path resulting from each angle and position must be considered separately, and hence graphical methods were more convenient and have been exclusively employed.

According to the theory of Rutherford and Soddy, each disintegrating atom of a radioactive material emitting α–rays sends out but one ray in a definite direction governed entirely by chance. When one is dealing with considerable quantities of emanation, during extended periods of time, the radiation may be regarded as one emitted uniformly in all directions, which assumption is made throughout the present investigation.

The graphical determinations of the "glass path" of the rays were made on a plane circular diagram drawn on a large scale (200 to 1) from the measurements of the wall thickness and diameter of the bulbs. The justification for the use of such a diagram is to be found in the fact that a *grand circle* of the sphere can always be passed through the path and the center of the sphere, and hence the relations holding for the grand circle will also hold for the sphere itself.

To obtain the lengths of paths radiating from points on the inner surface, any point is chosen and straight lines are drawn for each angle of five degrees, and the distance between the two intersections of the circumference is measured and recorded in terms of "air equivalence" in cm. It is evident that for points on the surface, one-half of the rays are at once lost into the glass wall.

As representative of points lying within the sphere (circle), ten concentric circles were drawn, the circle being divided into ten parts which would produce hollow spheres of equal volumes when rotated about an axis passing through the center. On each of these circles a point was taken, and paths, drawn at five-degree intervals, were measured and recorded

as described above. By this graphical method the air ranges were determined for all angles and positions. Each value was used to find the ionization by means of Bragg's[1] ionization curve, and thus an average value of ions per α-ray was obtained from emanation, radium A and radium C for each bulb employed. The way in which these values of i (ions) is then used will be better understood from Section 9.

5. General Applicability of the Thin-walled Bulbs

It may not be wholly out of place to digress somewhat from the main theme of this paper to point out here some of the advantages in the use of emanation contained in thin-walled bulbs, as a source of α-radiation, instead of a radioactive preparation. In the first place, emanation, in these small volumes, represents by far the most concentrated form of α-radiation that can be obtained. The emanation from two grams of radium could be contained in a bulb of 1.2 cubic mm. capacity and would possess three-fourths of the activity of the original radium salt, while occupying a volume about 400 times as small.

Such bulbs also provide a means of dividing the activity from a quantity of radium into several portions which can be used in ways in which one would not venture to employ the parent salt, the emanation having little or no intrinsic value. The main disadvantages are the short-lived activity of emanation, and the extreme fragility of the little bulbs.

As regards the ability of a bulb to emit an evenly distributed α-radiation in all directions, the regular outline of the light circle (cf. Section 3), as well as the constancy of the range for different positions and angles, would seem to give only favorable evidence. After making all corrections for absorption of the glass walls, the loss in ionization from this cause is estimated to be only about one-third of the theoretical total, even for the worst bulbs used; and the additional correction to be applied for absorption owing to the mercury contained in the capillary connection amounts to only 1 to 3 per cent.

[1] Mme. Curie: Traité de Radioactivité, II, p. 168.

6. *The Calculation of the Total Ionization*

As is well known, the direct measurement of the ionization produced by a strong source of α-radiation is impracticable by the electrical method, because a saturation current cannot be attained. For this reason it was necessary to employ an indirect method of calculation of the total ionization, depending on the following principles: The exact measurement of the amount of emanation contained in a bulb may be readily carried out by the γ-ray method.[1] The maximum air range of the α-rays from radium C may be measured by the method described in Section 3, which value, subtracted from 7.06 cm., gives directly the air equivalent of absorption of the glass for α-rays striking the wall normally. By application of the corrections set forth in Section 4, one obtains a set of values of the air ranges for rays emerging at all angles, for each of which the corresponding ionization per α-ray may be found from Bragg's ionization curve,[2] and by summation an average value is obtained for the total number of ions per α-ray. This value, multiplied by the total number of seconds, by the amount of emanation in curies, and by the number of α-rays per second per curie ($3 \times 3.4 \times 10^{10}$) is the *total number of ions formed during the whole experiment, a number bearing a close relation to the amount of ozone formed.*

The quantity of emanation was measured by the Vienna Standard, which is about 15 per cent. lower than that of Rutherford, on which the value of 3.4×10^{10} is based, and hence a correction of this amount had to be applied.

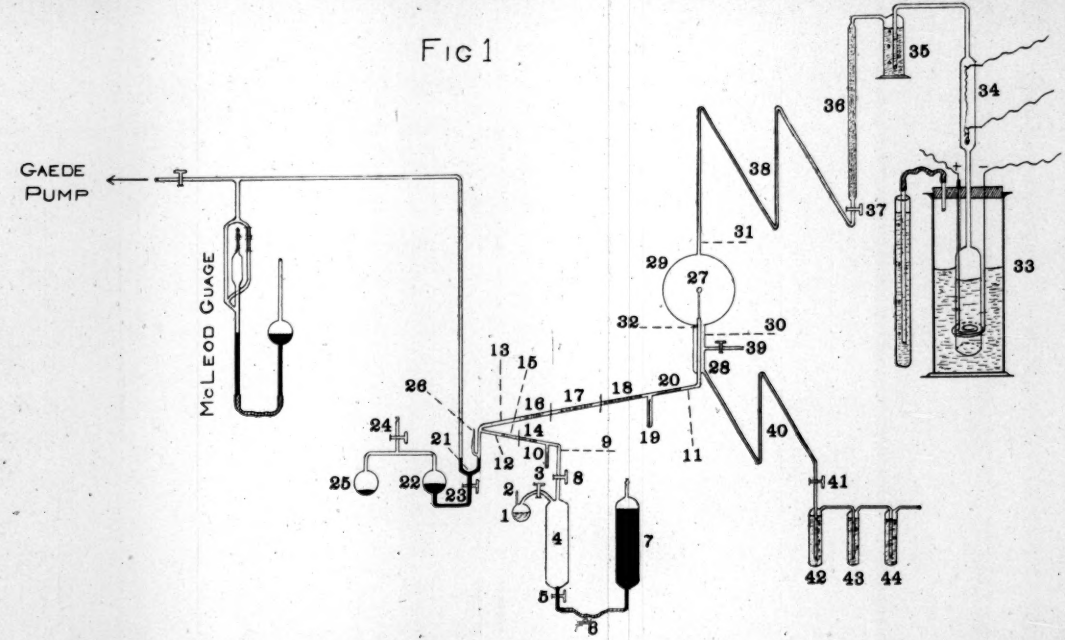
The quantity of ozone was determined chemically, from which the number of molecules is calculated on the basis of 2.69×10^{19} molecules per cc. of gas.

7. *The Purification of Emanation*

As a source of emanation, the Institut für Radiumforschung put at my disposal a 10 per cent. radio-barium chloride mixture containing 144 mg. of radium chloride. This salt, in weakly acid solution (about 50 cc.) was introduced into the 100 cc. side flask 1 (see Fig. I) through the side arm 2, which

[1] Mme. Curie: Traité de Radioactivité, II, p. 185.
[2] *Loc. cit.*

FIG 1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was then sealed off. The side flask 1 is connected through stopcock 3 with the 1-liter glass cylinder 4, which connects below through cock 5 and the rubber tube 6 with a second somewhat larger glass cylinder 7, and above opens into the purification system through cock 8.

During the slow collection of emanation (usually 6 to 10 days), cocks 5 and 8 are closed and cock 3 is open; 7 is filled with mercury; in 1 and 4 is a vacuum (except for water vapor). The large volume of cylinder 4 serves to reduce the concentration of emanation being collected, and thus diminishes the rate at which the solution in 1 is decomposed by the emanation. When emanation is ready to be taken, cock 3 is closed, and cocks 5 and 8 are opened, allowing the emanation, together with the hydrogen and oxygen produced by the decomposition of water in 1, to pass up into the purification system, which is first evacuated to 0.0001 mm. pressure, accompanied by gentle heating of the glass walls and the various purifying agents (as far as practicable) to remove the occluded gases.

The method of purification described here is a modification of the one worked out and employed in the laboratory of Mme. Curie by Prof. Duane and others. On account of its higher melting point, lead dichromate has been substituted for potassium dichromate, which tended to melt and clog the tube during the heating. Soda-lime has also been found preferable to fused potash as an absorbent for carbon dioxide. The tube 10 for the collection of water has also been added. The method does not seem to lend itself to the complete purification of emanation, but it is well suited to meet the present requirement, that is, a method capable of reducing the total gas volume within the limits imposed by the volumes of the small bulbs.

During the 6- to 10-day period of collection, more or less water distils out of the solution in 1 over into 4, where it collects on the surface of the mercury and later mounts with it through 8. To remove this water before it gets into the system beyond 9, a vertical side tube, half filled with calcium chloride, is put on at 10. The water is allowed to drop slowly

upon the calcium chloride and is absorbed, so that it remains in place, even when tube 10 is later filled with mercury. As shown in the figure, the purification tube between 9 and 11 is slightly inclined upwards along its entire length, in order to insure its complete filling with mercury as the emanation is displaced toward the upper end. The purifying agents are introduced loosely into the tube and are separated from each other by plugs of glass wool. The tubes, having been thus filled, are sealed into place in two sections, between 9 and 12 and between 11 and 13. At 14 is lead dichromate for the oxidation of the organic decomposition products, coming from the attack of stopcock grease by emanation; at 15 is soda-lime for the first absorption of carbon dioxide; at 16 and 17, again lead dichromate and soda-lime for a final treatment; at 18, two carefully reduced rolls of copper-wire netting and some freshly ignited copper oxide to burn out the hydrogen and oxygen gases; at 20, phosphorus pentoxide serves as drying agent. At 19 is a second vertical side arm, in which the emanation is condensed by means of liquid air, in order to be able to pump off the residual gases after the chemical purification is completed. To avoid loss of emanation, the pumping does not take place continuously nor directly into the pump, but by means of a mercury cut-off at 21, through which momentary connection only is made with the pump. Contamination from stopcocks is thus entirely avoided after the chemical purification. The rise and fall of mercury at 21 is controlled through cock 23 by means of an aspirator operated through cock 24. Flask 25 serves for the direct distillation of mercury into 22.

To carry out the purification, the gases out of 4 are first allowed to pass slowly over the heated lead dichromate; after repetition of this process mercury is allowed to mount as far as 12, after which the purification is completed in the absence of stopcocks. The glass at 14, 16 and 18, where it must be heated, for a time, to a dull red glow, should be protected externally by copper-wire gauze. The progress of the chemical purification may be followed by observing, from time to time, the readings of the small McLeod gauge at 26; after its

completion, a residual pressure of about 2 mm. usually remains. After cooling from one to one and a half hours in liquid air, the emanation is practically all condensed in 19, and the pressure is then reduced to that desired (a few thousandths of 1 mm.) by opening four or five times through 21 into a large volume, including the large McLeod gauge, which is used to determine the pressure after each operation. After removal of liquid air, tube 19 is gently warmed to drive out the emanation adsorbed by the glass wall and by the copper wire,[1] and the final pressure is then read on the capillary McLeod gauge 26, which is previously calibrated from the large gauge. In case the pressure is found sufficiently reduced, mercury is let in from 22 and passes slowly up through the purification tube and reagents until it just fills the neck of the little bulb 27. Some care is required during the first two hours in regulating the pressure so that mercury does not mount into the little bulb itself, from which it is removed with great difficulty on account of the narrowness of the capillary neck. This somewhat anomalous initial contraction, which has been observed by Ramsay[2] and others, has not yet been satisfactorily explained.

As shown in Fig. I, the emanation bulb 27 projects by means of an insealed joint at 28 into the center of a large glass sphere 29, in which the α-rays are fully utilized in all directions. This somewhat complicated arrangement was necessary in order to be able to employ the bulb *in loco*, thus avoiding the difficult operation of cutting it off and at the same time keeping its volume just filled with the emanation. After each series of experiments with a bulb, the sphere 29 is removed by cutting at 30 and 31; the small bulb is cut at 32, and the quantity of emanation contained in it is determined by the γ-ray method.[3]

8. The Formation and Measurement of Ozone

The apparatus shown in Fig. I enables one to work either

[1] A piece of copper-wire is introduced into the tube because it has been observed by Laborde and others (cf. Le Radium, 1909) that emanation is less easily vaporized at low temperatures from a *copper* than from a *glass* surface.

[2] Ramsay and Cameron: J. Chem. Soc., **91**, 1266 (1907).

[3] *Loc. cit.*

with still or with flowing oxygen, and to keep the ozone from continued contact with stopcock grease or mercury. The oxygen employed was electrolyzed from 1 : 2 caustic potash solution by means of the electrolytic generator 33. The oxygen passes first over a glowing platinum wire in tube 34 (25 cm. long and 3 cm. in diameter, etc.) to burn out the traces of hydrogen which get into the oxygen by diffusion. The oxygen passes next through concentrated sulphuric acid in wash flask 35, then through a 60 cm. layer of cotton batting (36) to remove dust particles, then through the stopcock 37, which remains closed during experiments with still gas; then follows a 1 mm. capillary tube (38), 50 cm. long, which hinders the diffusion of ozone back into the cotton during experiments with flowing gas, or to the stopcock in the case of still gas. The large glass cylinder 29, which constitutes the ozonization chamber, has a diameter of 12 cm. to insure the full utilization of the α-rays in all directions. At 39 is a stopcock and outlet tube used only in experiments at reduced pressure for pumping out the gas and for connection with a manometer. At 40 is again a long capillary way to prevent diffusion of moisture from 42 back into 29 during experiments with flowing gas. At 41 is a three-way cock which remains closed in experiments with still gas. In the wash flasks 42, 43 and 44 is a 7.5 per cent. neutral solution of potassium iodide to absorb ozone; 43 and 44 proved to be superfluous. Directly before the titration with 0.005 N sodium thiosulphate, the solution is acidified with 5 cc. of 1 N sulphuric acid.

During the first experiments, which were made with flowing gas, the apparatus was much simpler. The parts 36, 37, 38, 28, 40 and 41 were lacking. Tube 30, of broad diameter, delivered directly into the potassium iodide solution, consequently the oxygen in 29 was always moist. In later experiments it was sought to eliminate the irregularities in the rate of ozone formation by controlling more exactly the experimental conditions. With this object in view the apparatus was modified by adding the parts specified above, without, however, obtaining the desired result.

9. *The Experiments*

In Table II are given the results of several experiments with three different bulbs containing emanation. With Bulb A, two experiments (I and II) were made with moist, flowing oxygen; with Bulb B, three experiments (III, IV and V), under the same experimental conditions, except that the quantity of emanation was doubled. With Bulb C, five experiments were carried out, the first two (VI and VII) with dry, flowing oxygen free from hydrogen and dust; Number VIII on still oxygen of the same purity; Number IX on still oxygen at reduced pressure (one-fifth atmosphere); and Number X on still air, dry and dust-free.

The notation used in the table is as follows:

t = time of experiment in seconds.

E = integral mean of the quantity of emanation (expressed in curies) from the relation: $E = \dfrac{E(\text{initial}) - E(\text{final})}{\lambda t}$.

λ = the constant for the rate of decay of emanation = 2.085×10^{-6}.1/sec.

α = total number of α-rays emitted = $0.85 \times 3.4 \times 10^{10} E.t.$

i = average number of ions produced per α-ray (cf. Section 5).

N = total number of ions formed during the experiment = $\alpha.i$

M = total number of molecules of ozone formed = $2.69 \times 10^{19} \times$ number of cc. of gas.

Table II

	Bulb A	Bulb B	Bulb C
Diameter of bulb	1 mm.	2 mm.	1.5 mm.
Air range of bulb	5.9 cm.	5.0 cm.	5.0 cm.
E (initial)	0.032	0.064	0.0685
$i \times 10^{-5}$ for			
Ra A	1.21	0.76	1.00
Ra C	1.25[1]	1.28	1.50
Emanation	1.34	1.08	1.10
Total	3.80	3.12	3.60

[1] The value for Ra C is small here, because the first sphere used had a diameter of only ten cm., rendering the last cm. of range for Ra C ineffective.

Table II—(continued)

Bulb	Expt.	$i.\ 10^{-4}$	$E.\ 10^{-3}$	$a.\ 10^{-13}$	$N.\ 10^{-19}$	$M.\ 10^{-18}$	N/M	
A	I	5.67	2.92	4.7	1.8	3.65	5.0	
	II	8.64	2.52	6.3	2.4	9.1	2.6	
B	III	5.00	5.85	8.4	2.6	14.0	1.9	
	IV	8.67	5.07	12.6	3.9	6.3	6.2	
	V	8.60	4.23	10.6	3.3	9.1	3.6	
C	VI	4.0	6.47	8.0	2.7	4.2	6.4	
	VII	8.3	5.67	13.4	4.9	4.5	11.0	
	VIII	8.6	4.90	12.1	4.4	11.0	4.0	
					[4.7][1]		[107.0]	
	IX	14.0	3.37	13.0	0.6	0.44	13.4	($\frac{1}{5}$ atm. O_2)
	X	9.4	2.45	6.4	2.3	0.23	100.0	(1 atm. air)

10. Discussion of the Experimental Data

A comparison of the values N and M in the foregoing table brings to light two striking results of these experiments; first, that the order of magnitude of N and M is the same, their ratio N/M never falling below a minimum of about 2; and second, that large deviations are shown in the opposite sense. These deviations are the more notable in that they occur whether the experimental conditions are as closely parallel as possible, or are widely varied, and have eluded all attempts at their elimination. From the fact that M never appears greater than $N/2$, I am inclined to consider this maximum value for ozone formation as the theoretically correct one and to regard the lower values of M as resulting from a loss of ozone in some way.

As has already been pointed out, the recombination of ions to form ordinary oxygen would account for a loss of ozone, but this does not diminish our difficulty in explaining the deviations under apparently identical conditions. Nor will the assumption of deozonization by the rays themselves help in this regard; and, indeed, it is difficult to imagine that such a

[1] The bracketed numbers for an atmosphere of oxygen refer to the ionization calculated on the basis of 1 atmosphere, which is to show that the number 107 corresponds to the true value for air; that is, based on the quantity of emanation alone, the efficiency is equally low in both cases. But using the true ionization, it is equal to 13.4, a value comparable to that found in VIII, showing that the ionic efficiency remains constant.

process should take place to a measurable extent, if one remember that the concentration of ozone in these experiments never exceeds about 1 in 2000 parts by volume.

It remains to consider the possibility of some of the ozone having been chemically reduced before being titrated. Every precaution was taken to guard against this eventuality; but, at best, where such small quantities of a chemically active substance like ozone are to be handled during twenty-four hours or more, in a necessarily large apparatus, one can not be sure that such loss has not occurred.

But even after giving all due weight to the variations in the amount of ozone found, the order of magnitude remains practically unchanged, and the only plausible explanation is that a close relation exists between the extent of ozonization and of ionization, as stated above. Furthermore, the truth of this same principle will be demonstrated in the near future for a number of other gas reactions, which will lend additional confirmation to an ionic theory for gas reactions taking place under the influence of emanation.

11. *Conclusion. An Ionic Theory of Ozone Formation*

In the preceding paragraph it was shown that the limiting maximum value for the number of ozone molecules (M), formed by α-radiation, is equal to one-half of the total number of ions (N). This value for M lends itself to the establishment of a theory for the formation of ozone according to which the simplest mechanism would be based on the assumption that only the oxygen ions carrying one kind of charge (possibly the positive) combine with ordinary oxygen molecules, present in large excess, to form ozone molecules. The oppositely charged particles (possibly electrons) then act in reëstablishing electrical neutrality. The reason that the charge of one kind attaches itself to an oxygen molecule, instead of recombining at once with the opposite charge, is because the number of oxygen molecules present far exceeds the number of oppositely charged particles. Of course, the true mechanism may be quite another, but this one is suggested as being typical of the several hypotheses which might be ad-

vanced to fit the results, and between which it would not be possible to decide without further experimental data, the nature of which will be later indicated.

Unfortunately, our knowledge of the nature of gas ions is not, as yet, complete; but there is good reason to believe that most of the positive carriers in oxygen consist of singly charged atoms, which, at atmospheric pressure, are surrounded by, or are associated with, about 20 to 30 oxygen molecules. According to our theory the central ion is then capable of combining with one of the surrounding molecules to form ozone.

It is also possible to give a yet broader interpretation to these results, which does not involve the assumption that only one kind of ion acts primarily. Admitting that particles of either charge constitute centers of attraction or condensation for the molecules of gaseous oxygen, then, when two oppositely charged particles, either of which may be surrounded by a considerable number of oxygen molecules, come together to produce electrical neutrality, the molecular conglomerate in which the electrical centers of attraction have just been neutralized will undergo dissociation by the loss of molecules of ordinary oxygen, which action will proceed until the original molecular center has been reduced to the highest stable polymer of oxygen, namely, ozone. Neither this assumption, implying the immediate electrical neutrality of ozone, nor the first, assuming its generation by a positively charged particle, would be in agreement with Thornton's[1] observation that freshly formed ozone is *negatively* charged, so that it may be, after all, that only one kind of charge is evolved in the primary action, and that it is the negative instead of the positive. But however that may be, it appears quite certain that electrical charges are quantitatively involved in the formation of ozone by the α-rays.

In Experiment IX (Table II) the effect of reduced pressure in diminishing the ozone production is clearly demonstrated. At one-fifth of an atmosphere pressure, the whole layer of oxygen between the bulb and the outer wall of the ozonization chamber is equivalent to only $^6/_5$ of one cm. of oxygen

[1] W. M. Thornton; Phil. Mag., **21**, 632 (1911).

under atmospheric pressure, hence the greatest part of the energy of the α-rays is lost in the glass wall. Theory predicts, then, a marked decrease in ozonization, which is actually found to be the case. From Experiment X, one sees that the ozonization of air at atmospheric pressure is about equivalent to that of oxygen at $^1/_5$ of an atmosphere. Assuming that no oxides of nitrogen were titrated as ozone, this would indicate that the main activity of the oxygen ion is exerted toward the oxygen molecules, to the exclusion of nitrogen; and also that nitrogen ions have little activity toward oxygen; but too much weight should not be laid on this single experiment, particularly as forming a part of a series in which reproducibility is strikingly absent.

In conclusion, it may be remarked that the ionic theory of ozonization brings with it a host of interesting questions, which cannot be solved in the absence of further experimental data and of a means of obtaining more reproducible measurements. After this condition has been satisfied, one may hope to settle on a definite mechanism for the reaction. In this connection it would be interesting to know whether it is the gaseous *ion*, or the *atom*, which is chemically active. One might expect to throw some light on this question by producing an electrical field in the ozonization chamber, and by thus discharging a part of the ions, to ascertain what change would result in the quantity of ozone formed. It also seems possible that the ionic theory may be extended to modes of ozonization under the influence of other forms of radiant energy, such as silent and spark discharges and, possibly, ultraviolet light. The author hopes to be able to give this question fuller consideration in a subsequent paper.

It is a pleasure to express my thanks to Prof. Stefan Meyer and to Dr. Viktor Hess for their kindness in placing the splendid facilities of the Institut für Radiumforschung at my disposal, and for their friendly assistance in carrying out the foregoing experiments.

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NOTES ON THE ELECTRICAL METHOD OF MORSE AND GRAY[1] FOR THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN AND SULPHUR IN ORGANIC COMPOUNDS

By E. Emmet Reid

In the course of certain work on sulphur esters, a part of which has recently been published,[2] a number of sulphur determinations were made by the elegant method of Morse and Gray. This work led to certain minor modifications of the apparatus and method of procedure. It is thought that the publication of these modifications may make the method easier for some chemists and aid in the general adoption which the method so well deserves.

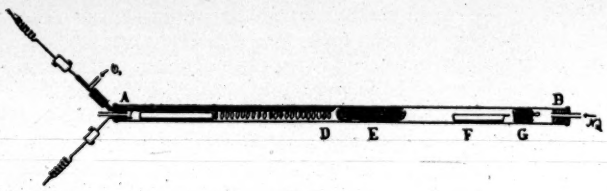

Fig. 1

The apparatus used is represented in Fig. 1. *AB* is a tube of transparent quartz 600 mm. long and of 17 mm. internal diameter. For this the ordinary hard-glass combustion tube may be substituted, but the use of the quartz tube has certain very great advantages. By the use of quartz, much time is saved in heating up and cooling down, before and after the combustion; the process may be regulated more exactly as any part of the tube may be heated or cooled quickly as the progress of the combustion demands; and the most refractory substances may be burned with ease and certainty since any desired temperature may be applied to the part of the

[1] This Journal, 35, 451.
[2] *Ibid.*, 45, 479.

tube containing the boat. Another great advantage is the ease and certainty with which the quartz combustion tube may be dehydrated. In one case the tube had been standing full of water. It was set up and completely dehydrated within an hour by heating with three Bunsen burners which were moved from time to time while a current of air was passed through it. In a quartz tube a roll of oxidized copper gauze may be quickly and surely dehydrated, owing to the high temperature which may be employed. The first cost of the tube (about $15, "duty free") is considerable, but its long life under severe conditions and the great time saving consequent to its use make it economical in the end.

From *A* to *D*, inside the combustion tube, is a small quartz tube, 300 mm. long and of about 4 mm. external diameter. In the present work this was of transparent quartz, but one of the opaque, so-called "electro-quartz," which costs very little, would serve the purpose just as well. The quartz tube has two advantages over the small porcelain tube employed by Morse and Taylor[1] and by Morse and Gray. It can be obtained much smaller and lighter than the porcelain tube and, for that reason, does not burden the stopper at the end of the combustion tube so seriously, and it can readily be bent. At 25 mm. from the end, this tube is bent to an angle of 45° and this bent end projects from the stopper. This bend is a great convenience as it gets the necessary connections on the end of this tube out of the way of the absorption train which has to be connected through the other hole in the same rubber stopper.

The wire used for the heating was 2 meters of No. 30 platinum wire, weighing 1.9 grams. This, when hot, had a resistance of 24 ohms and was used, on a 110-volt circuit, in series with an external resistance of 18 ohms, so that it took 2.6 amperes of current.

The arrangements of the tube and its contents were exactly as described by Morse and Taylor and later modified by Morse and Gray, except that quartz wool was substituted for asbestos for the two plugs at *E* and *G*.

[1] THIS JOURNAL, **33**, 590.

The Asbestos Plug.—In a number of analyses by the original method, the percentages of sulphur came more or less low. An investigation of all parts of the apparatus and process finally traced the error to the asbestos of the plug at *E*. Then the following experiments were made to test the magnitude of this error. The asbestos used in all of these was of the same lot and had been boiled for 4 hours with 10 per cent. hydrochloric acid and thoroughly washed.

Experiment 1.—In an analysis of nearly pure ethyl thiolbenzoate, in which 0.1395 gram of the ester was burned, the following results were obtained:

	Carbon	Hydrogen	Sulphur
Found	64.72	6.40	17.81
Calculated	65.03	6.06	19.33

The asbestos plug in the center of the tube was removed and boiled with pure water. The filtrate from this gave, with barium chloride, a precipitate weighing 8.7 mg., corresponding to 1.19 mg. sulphur, or 0.86 per cent. on the weight of the ester burned. This, added to the 17.81 above, gives 18.67 per cent. of sulphur, which is much nearer the theoretical.

Experiment 2.—An asbestos plug weighing 0.281 gram was placed in the center of the combustion tube and heated to a full red heat. One cc. of pure concentrated sulphuric acid was placed in a boat and gently heated while the acid vapors were driven through the tube by a slow current of air. This took 40 minutes, after which the heating and the current of air were continued 30 minutes longer. The plug was then removed and thoroughly extracted with boiling water. This was filtered and divided into two equal portions. With barium chloride, the one half gave a precipitate of barium sulphate weighing 11.7 mg., while the other half yielded 0.9 mg. alumina and a decided qualitative test for magnesium.

Experiment 3.—Thiobenzamide (0.2001 gram) was burned in the tube as in a regular analysis, the combustion taking 90 minutes. The oxides of sulphur were caught in 1.2229 grams of lead peroxide, but the carbon and hydrogen were disregarded. The sulphur found was 23.10 per cent., against 23.38

calculated. The central plug, which weighed 0.356 gram, was boiled with two portions of water, each portion being decanted through a filter. The filtrate, which was perfectly neutral, gave 3.1 mg. of barium sulphate, corresponding to 0.42 mg. of sulphur. or 0.21 per cent. on the weight of the substance burned. Adding 0.21 to 23.10 gives 23.31 per cent., which is sufficiently near the theoretical. After removing barium from the filtrate with sulphuric acid, 0.4 mg. of alumina and 1.9 mg. of magnesium pyrophosphate were found. Both of these precipitates must have been contaminated with silica, as the bases found are more than equivalent to the acid found.

Experiment 4.—Thiobenzamide (0.2012 gram) was burned and the oxides of sulphur caught in 1.4634 grams of lead peroxide. The percentage of sulphur found was 22.87. The asbestos plug gave, on extraction and precipitation, barium sulphate corresponding to 0.39 mg. of sulphur, 0.19 per cent. on the weight of the substance burned, making a total of 23.06 per cent. of sulphur.

These experiments, which were confirmed by others not given, show that under some circumstances, with some samples of asbestos, an appreciable amount of sulphur is retains by the plug in the middle of the tube. This sulphur remains in the asbestos as neutral sulphate, and may be recovered by boiling the plug with water and precipitating as barium sulphate. In several cases, after boiling with water, the asbestos of the plugs was further extracted with boiling dilute hydrochloric acid, but this treatment always failed to extract additional sulphates, showing that no basic sulphates insoluble in water are formed. The extent of the action of the oxides of sulphur on the asbestos evidently varies greatly, probably depending on the time and temperature of contact, the composition of the asbestos, and, possibly, other conditions. The amount of sulphur retained, as found in Experiment 3 above, was only 0.21 per cent., or scarcely more than the conventional analytical error, while in several other cases it was much greater. In the above experiments, a new plug of asbestos was used in each analysis. In case the same plug were used

over and over again, the material in the plug subject to attack by the oxides of sulphur might become exhausted and the plug then be incapable of retaining additional sulphur. The results published by Morse and Gray leave little to be desired. The possibility of error arising from the use of the asbestos led to the substitution of quartz wool as material for the two plugs. This was found to be perfectly suitable and gave excellent results.

The Lead Peroxide.—A quantity of pure lead peroxide was thoroughly mixed by repeated sifting and sealed up in small portions, each sufficient for one analysis. When an analysis was to be made, one of these tubes was broken and its contents emptied into the platinum boat. For a time this boat was weighed in a large stoppered weighing tube. The large surface and considerable weight of this glass tube are disadvantages and a considerable error can be made by inserting the stopper more or less rapidly and thus compressing the air in the tube more or less. It has proved perfectly satisfactory to weigh the lead peroxide in the open boat. In case sulphur only is to be determined, the contents of the boat need not be dehydrated, but if hydrogen also is to be estimated, the dehydration may be effected after weighing, just before introducing the boat into the combustion tube, or with the boat in the tube, before connecting the absorption train, or the amount of water given off by a weighed amount of the lead peroxide may be determined and the calculated amount deducted from the water found in the analysis. An experiment showed that all of the water present in lead peroxide is not given off till its final reduction.

In Experiment 3 above it will be noted that 1.2229 grams of lead peroxide satisfactorily absorbed 0.1156 grams sulphur trioxide, or 27 per cent. of the amount required to change it completely into lead sulphate. In this case the lead peroxide in the end of the boat first reached by the oxides of sulphur was completely converted into sulphate, while that in the other end of the boat was but slightly attacked. Experience has shown that 1.5 to 2 grams of lead peroxide is ample for the absorption of the amount of sulphur oxides

usually present in an analysis, while if the sulphur is low much less than this may be used. Besides the consequent saving of material, the use of the smaller amounts of the lead peroxide has two distinct advantages. First, it is easier to effect complete reduction in a thin layer. Second, a small error made in the blank determination affects an analysis less seriously when the amount of lead peroxide used in the analysis is relatively small. Even with the quantities here used, the weight of the lead peroxide is ten to twenty times that of the sulphur trioxide absorbed. In case hydrogen is to be determined in the same analysis, the smaller the amount of lead peroxide used, the less trouble there will be with its water content.

The Platinum Boat.—This was made from a strip of platinum foil 25 × 100 mm., formed into a semicircular trough, one end being closed by turning up a part of the foil. It is improved by welding a piece of platinum wire across the boat just inside the open end. This makes a little ridge which prevents the particles of lead peroxide from rolling out.

The Reduction of the Lead Peroxide.—Morse and Gray advise reducing the lead peroxide by heating in a current of nitrogen. This was tried and found to be perfectly satisfactory. However, it involves some trouble in the preparation and storage of the nitrogen. The use of the quartz combustion tube greatly simplifies this operation. When the combustion is complete, the absorption train is removed and two strong Bunsen burners with wing tops are placed under the part of the combustion tube containing the lead peroxide boat while the flame of a third burner is directed down on the tube just over the boat. In the analyses given below this heating was continued exactly two minutes. The progress of the reduction can be watched and is practically complete when the whole mass has reached a good red heat. As soon as the reduction is complete, all of the burners are removed at once and the whole cools so quickly that there is no opportunity given for the formation of appreciable amounts of intermediate oxides. This method of reduction is troublesome in a glass tube, since the high heat is apt to soften the

tube sufficiently for the edge of the platinum boat to stick to the glass at some point. Very good results may be gotten without the quartz tube by supporting the platinum boat on a triangle and placing on top of the boat a piece of sheet iron just large enough to cover it. The flame of a blast lamp is directed down on to this piece of sheet iron while the boat is heated from below by a Bunsen burner. The heating is begun at the closed end of the boat while the operator watches the process from the open end and moves the burner along as is required. About two minutes is required for the whole reduction. The results are satisfactory but more or less of the lead monoxide is apt to fuse and cause difficulty in cleaning the boat.

The following three blanks were made to determine the loss in weight of the lead peroxide used in this work. As, in making the blanks, the tube and boat were quite cold when the heating was begun, the heating took 2.5 minutes each time instead of the two minutes in the regular analyses where the tube and boat were already quite warm. The reheating was conducted in exactly the same way and for the same time.

	1	2	3
Weight of peroxide taken, grams	2.7888	2.3020	2.8546
Loss on heating first time	0.1948	0.1610	0.1994
Loss on heating second time	0.0003	0.0001	0.0002
Loss on heating third time	0.0000	....	....
Loss for 1 gram	0.06996	0.06999	0.06992

It is evident that the reduction was practically complete in the first heating. The loss of weight, on heating, was taken as 0.06996 gram for 1 gram of this lead peroxide. The calculated loss is 0.06697, from which it appears that this material contained 3.0 per cent. of water.

Test Analyses.—The following are five consecutive analyses made to test the method in its present form. The carbon and hydrogen were disregarded. The substance burned was a very pure sample of thiobenzamide which should contain 23.38 per cent. of sulphur:

Number	1	2	3
Weight of sample	0.2038	0.2050	0.2388
Peroxide used	2.0781	2.8059	1.8703
Calculated loss	0.1456	0.1963	0.1308
Change in weight	—0.0282	—0.0769	+0.0086
Sulphur trioxide	0.1172	0.1194	0.1394
Sulphur	0.04694	0.04782	0.05583
Sulphur, per cent.	23.03	23.32	23.38

Number	4	5
Weight of sample	0.2786	0.2176
Peroxide used	2.1906	1.9926
Calculated loss	0.1533	0.1394
Change in weight	+0.0088	—0.0132
Sulphur trioxide	0.1621	0.1262
Sulphur	0.06492	0.05054
Sulphur, per cent.	23.30	23.23

By "change in weight" is meant the difference in the weight of the boat containing the lead peroxide before the analysis and after the reduction. In some cases (Numbers 3 and 4) the boat gained in weight as the weight of sulphur trioxide absorbed during the combustion was greater than the loss of weight due to the reduction of the dioxide to the monoxide. The weight of sulphur trioxide is taken as the algebraic sum of the "calculated loss" and the "change in weight."

In these analyses nitrogen or air was used to drive the substance through the tube to meet the oxygen which was passed in through the small tube. The burning was quite slow, occupying from 90 to 120 minutes, but required comparatively little attention, as a burner was placed near enough to the boat containing the substance to cause the compound to volatilize slowly, the heat being very gradually increased from time to time. Later work, shortly to be published, along somewhat similar lines indicates that the time taken for these combustions was longer than necessary. The gases issuing from the tube were tested from time to time with a glowing splinter and the admission of oxygen so regulated that this test should show an excess of oxygen. In spite of this precaution, complete combustion of the carbon was not secured in Numbers 3, 4 and 5. In Numbers 3 and 4 a small amount of soot was

deposited in the end of the combustion tube beyond the boat containing the lead peroxide, while in Number 5, unburned vapors were observed at one time. The noteworthy thing is that the sulphur may be completely burned and satisfactorily absorbed even when the carbon is not. It is well known that hydrogen will burn before carbon when the temperature is low or the oxygen insufficient. The beauty of the method is that the two oxides of sulphur are absorbed with equal ease. It seems likely that even vapors of sulphur would be absorbed by the lead peroxide and, if they were so absorbed, they would be transformed to lead sulphate in the final heating and give a correct weight. The case is quite different with sulphur from what it is with carbon, of which only the higher oxidation product can be absorbed while the lower, carbon monoxide, escapes completely.

The Simultaneous Estimation of Carbon, Hydrogen and Sulphur.—The above results show that the estimation of sulphur, by this method, is easy and satisfactory. In order that the lead peroxide may have a good opportunity to absorb completely the oxides of sulphur passing over it, the velocity of the current of gases passing over the boat must be kept down, while to insure the complete combustion of the carbon a considerable excess of oxygen must be present at every moment during the operation. This necessitates the admission of a large amount of oxygen and close supervision. Morse and Taylor call attention to this and say: "Careful management is required even in the combustion of such substances as sugar, when the roll of wire gauze is omitted." A small amount of a solid oxidizing agent, such as copper oxide, serves as an equilibrator, or reservoir of oxygen, which may be drawn open at any moment when there may happen to be an excess of combustible gases, to be replenished the next moment by an excess of oxygen.

In order to test the estimation of carbon with the same arrangements used above for sulphur, the following analyses were made, little care being taken with the hydrogen:

Substance	Weight taken	Time Minutes	Carbon Per cent.	Hydrogen Per cent.
Benzoic acid	0.1661	117	68.62	5.39
Benzoic acid	0.1138	105	68.61	5.43
Calculated	....	..	68.82	4.96
Sugar	0.1176	63	40.78	6.65
Sugar	0.1527	91	41.24	6.52
Calculated	....	..	42.08	6.48

It will be noticed that in the case of the benzoic acid the percentage of carbon found is satisfactory, while, in the case of the sugar, the carbon is much too low, though the hydrogen is correct. The specimen of sugar was of exceptional purity, such as is used for osmotic pressure work in this laboratory. The result for carbon in ethyl thiobenzoate, as found in the analysis given above in Experiment 1, was fair. The explanation is simple. The benzoic acid and the ester, when heated by a burner in a fixed position, both give off vapors at a regular rate and these vapors are properly burned by the steady current of oxygen meeting them, but the sugar, no matter how carefully it is heated, burns in stages, giving off, more or less suddenly, considerable quantities of combustible gases. In the second of the analyses of sugar, pure oxygen was led in at both ends of the tube and the combustion carried on with great care.

In order to test the effect of inserting the roll of oxidized copper gauze, the following combustions were made with the same sample of sugar and with all the rest of the apparatus exactly the same. In order to protect the quartz tube, the roll of copper gauze was placed in a platinum boat. A slight white coating forms on the tube over the copper gauze. The time of burning was much less than in those above, occupying about 20 minutes:

Weight taken Gram	Carbon Per cent.	Hydrogen Per cent.
0.1698	42.16	6.64
0.1990	42.15	6.55
0.2003	42.22	6.58
Calculated	42.08	6.48

This test is superfluous except to bring out the contrast

in the results with carbon, using the same apparatus with and without the copper roll. The results by the electrical method, reported by Morse and Taylor in the original paper, are all that could be asked, but even these are far surpassed in recent analyses of sugar, by the same method, by Morse and others,[1] in which the variations in the percentages of carbon and hydrogen found are kept down to 0.03 per cent.

The results published by Morse and Gray for the *simultaneous* estimation of carbon, hydrogen and sulphur leave little to be desired. The experiments above given show that all three elements can be simultaneously determined, but that, particularly with substances that burn irregularly, it would be more certain, and consume less time, to make two combustions, one with exclusive reference to the carbon and hydrogen and the other with reference to the sulphur. The sulphur determination may be carried out as above, while for the carbon and hydrogen a boat containing copper gauze or lead chromate should be inserted in the center of the combustion tube. The sulphur oxides which escape from these metallic oxidizing agents may be absorbed in the tube filled with lead peroxide and asbestos, as described by Morse and Gray, for the absorption of the oxides of nitrogen.

The Absorption of the Oxides of Nitrogen.—Morse and Gray advise for this purpose lead peroxide mixed with asbestos in a tube which is kept at 175°. For maintaining the tube at this temperature they devised an efficient electrical heating arrangement, the construction and use of which they fully describe. A convenient substitute for this has been found in a brass block 50 × 50 × 360 mm. having a circular hole 25 mm. in diameter through its longest axis. This was covered by asbestos and heated by a Bunsen burner, while a thermometer dippping into fusible metal in a hole drilled in the block gives the temperature. This was copied from the aluminium block described by Richards. This block has proved convenient for many other operations.

The results of this work are summed up in the following

[1] THIS JOURNAL, **45**, 555.

slightly modified form of the electrical method of Morse and Gray for the estimation of sulphur in organic compounds.

A combustion tube of transparent quartz 600 × 18 mm. is used, though one of hard glass can be made to serve. In the end *A* is inserted a two-hole rubber stopper, through one hole of which passes a small quartz tube of about 4 mm. external diameter. This may be of transparent quartz or of the much cheaper "electroquartz." This tube is 300 mm. long and, at a point 25 mm. from the end, is bent to form an angle of 135°. The bent portion projects through the stopper. To the outer end of this is fastened a T-tube into the other side of which is fused a platinum wire. This wire must be large enough to carry a current of some 3 amperes without heating. The wire passes through the T-tube, through the small quartz tube, and connects at the end of the latter with one end of the fine platinum wire which forms the heating coil. This consists of 2 meters of No. 30 platinum wire which is wound into a spiral about 12 mm. in diameter which is supported on the small quartz tube. For a distance of about 125 mm. from the stopper this wire is coiled tightly around the small quartz tube and its end is joined to a rather stout platinum wire which passes through the stopper. These close coils are so spaced as to keep the lead peroxide in the boat just below them nearly, but not quite, up to its decomposition point. The resistance of the heating coil is about 24 ohms and a current of about 2.6 amperes is required to keep it at the proper temperature.

A piece of platinum foil 100 × 25 mm. is taken and across it, about 1 mm. from the end, is welded a piece of platinum wire. The other end is notched and turned up. The foil is then bent to form a semicircular trough to fit inside the combustion tube.

At *E*, just beyond the end of the small quartz tube, is placed a plug, about 75 mm. long, of quartz wool. Just over this portion of the combustion tube is suspended a shield of thick asbestos board, and under it is placed a strong burner with a wing top. The plug of quartz wool at *G* contains a loop of platinum wire by which it may be withdrawn when the boat

is to be inserted. The portion of the combustion tube containing the heating coil is provided with a close fitting cover of asbestos board having a narrow slit through which the coil may be observed.

A quantity of pure lead peroxide is thoroughly mixed by repeated sifting and sealed up in 1–2 gram lots. A blank determination is made on this to determine its loss in weight when reduced to the monoxide. To do this the lead peroxide is weighed into the platinum boat which is then placed in the quartz combustion tube. Two burners with wing tops are placed under the boat and the flame of a third is directed down on the tube just over the boat. The heating is continued till all parts of the peroxide have reached a full red heat, which requires about 3 minutes, when all the burners are removed and the boat cooled quickly. Excessive heating is likely to fuse some of the lead monoxide and make it difficult to remove it from the boat. The resulting monoxide should be of a uniform pure yellow color. The boat is reweighed and the loss in weight, on reduction, calculated for 1 gram of the peroxide.

When a determination is to be made, 1–2 grams of the lead peroxide is weighed into the boat, the powder being spread out as much as possible. Using the results of the blank, the loss in weight, on reduction, is calculated. The weight of the boat and its contents is diminished by this amount and the remainder subtracted from the final weight to find the weight of sulphur trioxide absorbed during the combustion.

The platinum boat is put in place, the quartz plug at *E* heated very hot and the platinum coil brought to a bright red before inserting the boat containing the substance to be burned, after which the burner under the plug *G* is lighted. A slow current of oxygen is admitted through the small quartz tube. This is so regulated that an excess of oxygen is always present in the gases that issue at *A*. A third burner is held in the hand, or placed in a suitable position, to heat the boat at *F* so as to volatilize slowly the substance to be burned, the vapors from which are driven through the quartz plug at *E* by a slow current of air, or nitrogen, admitted at *B*. This heating must be cautiously done, else combustible vapors may be evolved

more rapidly than can be burned by the limited amount of oxygen present at any one time in the forward part of the tube. The most refractory substance may be completely burned by using the high temperature permitted with a quartz tube, and if necessary, admitting oxygen at *B*.

In order to insure complete absorption of the oxides of sulphur by the solid absorbent, the velocity of the current of gases passing over the lead peroxide must be kept low. Care is required in the regulation of the currents of oxygen and air so as to insure complete combustion and yet not to sweep unabsorbed oxides of sulphur out of the tube. However, the sulphur may be satisfactorily burned and absorbed when all of the carbon is not. The burning of 0.2 gram of substance may be done in about 1 hour.

When the combustion is complete, the platinum boat is heated for the reduction of the lead peroxide as above described.

This work was done with the approval and encouragement of Professor Morse and is now published with his approval.

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SOME TRANSFORMATIONS OF METASULPHAMIDOBENZOIC ACID UNDER THE INFLUENCE OF HEAT[1]

BY ROKURO NAKASEKO

This acid was first described by Limpricht and Uslar[2] as sulphobenzamic acid, $C_{14}H_7NS_2O_8$. They obtained it by heating sulphobenzamide or ammonium ethyl sulphobenzoate with potassium hydroxide. Sulphobenzoic acid, which was well dried over a free flame, was mixed in a tubulated retort with 2.5 times its weight of phosphorus pentachloride and heated to 150°. The reaction product was poured into cold water and the oil that sinks to the bottom was washed with water. It was then carefully dropped into concentrated aqueous ammonia. After standing for twelve hours the sulphobenzamide

[1] Cf. note, THIS JOURNAL, **47**, 1.

[2] Ann. Chem. (Liebig), **106**, 36, 37, 42–46 (1858).

completely separated out. It was now washed with cold water, made to a thick paste with concentrated potassium hydroxide, and heated several hours on a water bath. The clear solution of the potassium salt of sulphobenzamic acid was diluted with water and acidified with hydrochloric acid, whereupon a voluminous precipitate of the sulphobenzamic acid was thrown down. The authors characterize the acid in the following words:

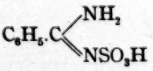
"Sulphobenzamic acid separates out from hot aqueous solution in scales resembling potassium chlorate; it is hardly soluble in cold water, more easily in ether, and easily in alcohol. It melts above 200°. If it is kept ten minutes over an alcohol lamp in the melted state, it solidifies, on cooling, to a brown tarry mass, easily soluble in water. If the sulphobenzamic acid is distilled with 1.5 equivalents of phosphorus pentachloride, there is found in the distillate, besides phosphorus oxychloride, chlorinated cyanophenyl in considerable quantity, and the chloride of chlorobenzoic acid in smaller quantity. Besides these, there is also found in smaller and very variable amount a chloride of an acid which is easily soluble and appears to be isomeric with sulphobenzamic acid. On evaporation of the absolute alcoholic solution of this latter acid there remains a syrup; if, however, it is left standing over sulphuric acid it solidifies to a wartlike, crystalline mass, which is easily soluble in water and alcohol. Its barium salt is easily soluble and crystallizes in small, concentrically united needles. The barium was determined in the salt dried over sulphuric acid. It was found to contain 22.3 per cent. of barium. The formula for the barium salt of suphobenzamic acid, containing 2 molecules of water, requires equally 22.3 per cent. of barium. The lead salt is easily soluble and difficultly crystallizable. The silver salt was obtained as a brown, moderately hard, crystalline crust; the analyses gave 34.2 per cent. and 34.9 per cent. silver, whereas the formula for the salt of sulphobenzamic acid requires 35 per cent. If equivalent amounts of phosphorus pentachloride and ordinary sulphobenzamic acid are heated in a retort, there remains a yellow mass from which ether extracts the chloride of the above described isomeric

acid, leaving an amorphous modification of sulphobenzamic acid as a white, powdery mass. The easily soluble isomeric acid was prepared from the chloride and analyzed for carbon and hydrogen. The calculated percentages are C = 41.7, H = 3.5, while the percentages found were C = 40.9, H = 3.7. The lead salt was then prepared and analyzed; the calculated percentage of Pb = 48.9; found = 48.8 and 48.9.

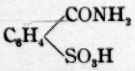
"The amorphous sulphobenzamic acid appears under the microscope in the form of small spherules in which nothing crystalline is to be discerned. It is insoluble in water, alcohol and ether, even on continued boiling. However, if it is heated with water in a sealed tube to 170°–180° it is reconverted into ordinary sulphobenzamic acid. The determination of carbon and hydrogen in the amorphous acid gave the results: C = 41.4, H = 3.4, while the calculated percentages are C = 41.7, H = 3.5. The amorphous sulphobenzamic acid is formed whenever the crystallized acid is heated with more than one equivalent of phosphorus pentachloride. It is not difficult to obtain the amorphous acid in a pure state. The salts are not crystallizable so far as our experiments show."

Thus, according to Limpricht and Uslar, there seem to be at least three different acids of the composition $C_7H_7SO_4N$.

Engelhardt[1] thought he obtained sulphobenzamic acid by the action of sulphur trioxide upon benzonitrile, but it was shown by Eitner[2] that the former was misled in this conclusion by an insufficient determination of the constituents of the resultant compound. Eitner's thorough investigation shows that the compound thus obtained is sulphobenzamidinic acid,



and not sulphobenzamic acid,

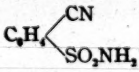


[1] Ann. Chem. (Liebig), **108**, 343 (1858).
[2] Ber. d. chem. Ges., **25**, 461 (1892).

Remsen and Palmer[1] obtained the *m*-sulphamidobenzoic acid identical with the sulphobenzamic acid of Limpricht and Uslar by oxidizing *m*-toluenesulphamide with potassium permanganate. "It fused at 235° (uncorrected), at the same time suffering partial decomposition." They also made it by oxidizing *m*-toluenesulphamide with chromic acid mixture.

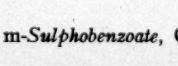
Remsen, Noyes and Walker[2] made the same compound by oxidizing *m*-toluenesulphamide with an alkaline solution of potassium ferricyanide. The potassium salt was purified by evaporating the solution to dryness and treating the residue several times with strong alcohol to remove any of the unoxidized amide which it contained. It was then dissolved in water, the acid was precipitated with hydrochloric acid, and recrystallized from hot water. Purified in this way it fused at 246°–247° (uncorr.).

W. Jones[3] used in his investigations the *m*-sulphamidobenzoic acid prepared for the most part by a slight modification of the method of Limpricht and Uslar. He also used the acid obtained by saponification of *m*-sulphamidobenzonitrile,



The latter compound was made by heating the mixture of *m*-sulphobenzoic diamide and phosphorus pentachloride.[4] Jones says no method is better adapted to the preparation of the *m*-sulphamidobenzoic acid than the latter one.

Guided by the results of all these investigators, I proceeded as follows:

Acid Potassium m-*Sulphobenzoate*,  .—Benzoic acid is fused, and after solidification, reduced to a fine powder and introduced into a large balloon flask. Sulphur trioxide is distilled into this balloon flask from a retort containing fuming sulphuric acid. The powdered benzoic acid is

[1] Ann. Chem. (Liebig), **4**, 144 (1882–1883).
[2] *Ibid.*, **8**, 188 (1886).
[3] Private communication.
[4] Ann. Chem. (Liebig), **108**, 33 (1858). Ber. d. chem. Ges., **9**, 427 (1876).

soon liquefied by the sulphur trioxide with evolution of considerable heat. When the whole mass is completely liquefied a few cc. of fuming sulphuric acid are added, and the whole heated over a small flame for several hours. The reaction product, which contains, besides the original materials which escaped action, *m*- and *p*-sulphobenzoic acids[1] is poured into cold water and left standing overnight. The greater part of the unchanged benzoic acid is thus precipitated. The filtered solution is neutralized with calcium carbonate and filtered. The filtrate contains the crude calcium salt of *m*-sulphobenzoic acid, perhaps mixed with some *p*-sulphobenzoate of calcium. It is subjected to double decomposition by addition of a solution of potassium carbonate. The potassium salt is now filtered and concentrated and acidified with half the equivalent quantity of hydrochloric acid. On cooling, the difficultly soluble acid potassium salt separates out, which is then dried and extracted with 95 per cent. alcohol for the purpose of removing the last trace of benzoic acid, and repeatedly purified by recrystallization from water.

I know no convenient method to test for the presence of *p*-sulphobenzoic acid in *m*-sulphobenzoic acid. I therefore proceeded with the product thus obtained, on the assumption that it is pretty nearly pure acid potassium *m*-sulphobenzoate.

m-*Sulphobenzoic Dichloride*, $C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}$.—This compound is made from the dried acid potassium salt of *m*-sulphobenzoic acid by treating it with two equivalents of phosphorus pentachloride. The oil thus obtained is well washed with water and treated with dilute ammonia in the cold to convert it into

m-*Sulphobenzoic Diamide*, $C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases}$.—This substance melts at 178° (uncorr.), while Jones gives it as 176°. It is now treated with phosphorus pentachloride to convert it first into

[1] Ann. Chem. (Liebig), **178**, 279 (1875).

m-*Sulphamidobenzonitrile Hydrochloride*, $C_6H_4\begin{cases}C(Cl)=NH\\SO_2NH_2\end{cases}$,

which gives, when dissolved in warm water,

m-*Sulphamidobenzonitrile*, $C_6H_4\begin{cases}CN\\SO_2NH_2\end{cases}$.—This substance is now boiled for several hours with dilute sodium hydroxide and then acidified with hydrochloric acid, whereupon there separates out as a white, voluminous precipitate

m-*Sulphamidobenzoic Acid*, $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$.—This substance is now repeatedly purified by recrystallization from water and is found to melt always at 237°–238°. Noyes, Walker and Jones found the melting point of this substance to be 248°, while Palmer found it previous to them to be 235°. I made my substance by the above method, which is recommended by Jones as the best one, in separate portions and at different times, and always found it to melt at 237°–238°, after repeated recrystallization. To eliminate the possibility that my thermometer might have been wrong, I compared it with two other standard thermometers and found that they agreed. Now between the melting point of my substance and that of Noyes, Walker and Jones, there is a discrepancy of 10°. To clear up this point, I made the ammonium salt of *m*-sulphamidobenzoic acid and purified it by several recrystallizations. The purified ammonium salt was then converted into the lead salt, and again purified by several recrystallizations. The purified lead salt was then subjected to double decomposition with dilute sulphuric acid. The free *m*-sulphamidobenzoic acid thus obtained was then repeatedly recrystallized and found to melt at 237°–238°. To further insure the purity of the substance I boiled it for several hours with dilute sodium hydroxide in order to saponify any trace of *m*-sulphamidobenzonitrile which might be present as an impurity. After this treatment the free acid was reprecipitated by hydrochloric acid and repeatedly recrystallized. It still

melted at 237°–328°. At present I do not know how to explain this serious discrepancy. Probably it may be due to the presence or absence of the *p*-sulphamidobenzoic acid in either of these products.

The Quantitative Study of the Change That Takes Place on Melting m-*Sulphamidobenzoic Acid*

Although the melting point of the *m*-sulphamidobenzoic acid is 237°–238°, it can be melted at a temperature considerably lower than this, if it is kept long enough at that temperature, as is seen from the following experiments:

A sample of the acid was dried by heating it in an air bath at 140° for two hours, and then put into 3 specimen tubes, weighed and heated for four hours at 210°–215°; it did not melt at the end of this time. On slowly raising the temperature to 220° it melted completely. As was shown also by all the following experiments, whenever the acid is fused there is produced a very minute quantity of a sublimate in the form of flat, shiny needles. The quantity of this sublimate was always so inconsiderable that I was never able to collect a sufficient amount of it to determine its melting point. After complete fusion, the contents of the specimen tubes were cooled in a desiccator, weighed, dissolved in water, evaporated on a water bath, dried in an air bath at 100°–110°, and then weighed. The drying operation was continued thirty hours, during which six to ten weighings were made to make sure of the continual loss of weight:

	Substance taken	Change in weight on fusion Per cent.	Gain in weight after dissolving and drying Per cent.
I	0.8915	—0.11	4.41
II	0.9884	+0.20	3.06
III	0.8528	—0.12	4.95
IV	2.0515	—0.12	6.60
V	1.8676	—0.09	5.94

The percentage of the increase in weight after dissolving in water and subsequent drying never reaches the amount—8.95 per cent.—which would be expected if the substance were simply and completely converted into acid ammonium

m-sulphobenzoate. Neither did the loss in weight cease after thirty hours of heating. Still, to convince myself that the continual loss of weight was not due to the continual decomposition by heat, I made another series of similar determinations in which the drying operation was carried on exclusively on a water bath. The results are as follows:

	Substance taken	Change in weight on fusion Per cent.	Gain in weight after dissolving and drying Per cent.
I	2.7102	—0.06	2.76
II	0.6736	0.00	4.94
III	0.8135	—0.03	5.04

These two series show conclusively that the fusion product of *m*-sulphamidobenzoic acid does not go over completely, to say the least, into ordinary acid ammonium *m*-sulphobenzoate. I use the adjective "ordinary" because I will show later that I obtained a new modification of the acid ammonium *m*-sulphobenzoate, together with a new modification of *m*-sulphobenzoic diamide from the fusion product of *m*-sulphamidobenzoic acid. But before going further, I will give here a typical example of the continual loss in weight on drying the solution of the fusion product of *m*-sulphamidobenzoic acid:

No. V of the First Series Given Above

Weight of substance taken, 1.8676 gram

Temperature of the air bath	Duration of drying Hours	Weight of the evaporating dish + the reaction product
100°	4	16.6325
100°	5	16.6170
100°	2.5	16.6150
100°	4	16.6110
100°	2	16.6095
95°–105°	6	16.6060
95°–105°	7	16.6052
105°	7	16.6042
107°	6	16.6040

The increase in weight in the last weighing was thus 5.94 per cent. The calculated increase of the acid ammonium salt is 8.95 per cent.

Experiments with the Fusion Product of m-*Sulphamidobenzoic Acid*

Twenty-three grams of the acid were heated in the air bath to 222°, and kept at this temperature for three hours, at the end of which it had melted to a dark liquid. After cooling and solidifying, the hard, brittle mass was reduced to a powder, during which operation the substance eagerly attracted moisture from the atmosphere. The powdered substance was now digested with ether, which made it sticky and extracted from it an inconsiderable amount of dirty matter. The residue was then treated with acetone which had been freshly distilled at 58°–59°. The extraction with acetone was repeated seven times and from the concentrated acetone extract there separated out in small quantity some fine crystals which were colored a dark reddish yellow. A few drops of absolute alcohol removed the coloring matter and left the crystals in clean colorless form. These crystals gave off ammonia on treating with sodium hydroxide in the cold, and blackened suddenly at 265° without melting. The solution of these crystals was strongly acid, and gave acid barium *m*-sulphobenzoate on treating with barium carbonate and subsequently acidifying with hydrochloric acid. The dirty matter obtained from the ether extract gave no ammonia with sodium hydroxide in the cold; was easily soluble in water and had a strong acid reaction; gave off ammonia on boiling with sodium hydroxide. The residue, after successive treatment with ether and acetone, was digested with 95 per cent. alcohol on the water bath; the brownish alcoholic filtrate gave on concentration fine, colorless, silky needles, which were not very soluble in water. When dry, these needles did not melt even at 274°. On treatment with a solution of potassium carbonate ammonia was given off.

But the main part of the fusion product remained undissolved through all these treatments; this final residue constituted probably 99 per cent. of the whole fusion product. It was now dissolved in water and added to the aqueous solution of the fusion product used in the two preceding series o-experiments. The moderately concentrated aqueous soluf

tion was subjected to slow evaporation in a large bell jar over sulphuric acid. A portion of the constituents gradually crept up the wall of the vessel and there formed a thick crust, while another portion formed on the bottom of the vessel stout, thick, transparent plates, some of which were in the shape of regular hexagons. These crystals were now picked out from the mother liquor and rinsed with cold water. In this manner the main part of the fusion product of *m*-sulphamidobenzoic acid was roughly separated into three fractions, namely:

A. The substance that creeps up the wall
B. The stout, transparent hexagonal plates
C. The mother liquor

A. The Substance that Creeps up the Walls of the Vessels Containing the Solution of the Fused Metasulphamidobenzoic Acid.—It is dissolved in water and treated with barium carbonate in the cold. There is a slow evolution of carbon dioxide and the originally acid solution becomes, first, neutral, and after about two hours gives off ammonia which can be recognized with moist litmus paper as well as by its smell. The liquid is now filtered, by which operation the colored impurities are left behind with the excess of barium carbonate, and a nearly colorless filtrate is obtained. This is now strongly acidified with hydrochloric acid and concentrated over the water bath. On cooling, the characteristic square plates of acid barium *m*-sulphobenzoate, $\left(C_6H_4\begin{matrix}COOH\\SO_3\end{matrix}\right)_2 Ba + 3H_2O$, separate out. The analyses gave the following results:

Determination of Water of Crystallization

	Substance taken Gram	Temperature of the bath	Loss in weight Per cent.
I	0.5477	125°	9.53
II	0.4265	125°	9.29
Calculated for the above formula			9.12

For the purpose of verification the acid barium *m*-sulphobenzoate was made from the acid potassium salt. The result of analysis was:

III. 0.15 gram substance suffered, on heating at 130°, a loss of 9.07 per cent.

Determination of Barium

	The dry substance taken Gram	Ba found Per cent.	Ba calc. Per cent.
IV	0.3869	25.06	25.41

All the properties of the acid barium salt thus obtained from the fusion product exactly agreed with those described by Mitscherlich[1] and Otto[2] for the acid barium *m*-sulphobenzoate except in one point, namely, Otto stated that the acid salt is more easily soluble in hot water and alcohol than in cold water. I convinced myself, however, by special experiments, that Otto's statement is erroneous on this point and that the acid barium *m*-sulphobenzoate is insoluble in alcohol, both hot and cold.

V. Another portion of the substance that creeps up the walls of the vessel was dried at 145° for three hours and titrated with an alcoholic solution of potassium hydroxide and litmus. The substance taken weighed 0.3150 gram. The acidic hydrogen found was 1.54 per cent., while the acidic hydrogen calculated for acid ammonium *m*-sulphobenzoate is 0.46 per cent.

B. The Stout Transparent Hexagonal Plates.—These crystals are very easily soluble in water and also easily crystallizable from concentrated solutions in clean and thick plates. If they are kept in the air they lose water of crystallization and crumble to pieces. They are soluble in boiling 95 per cent. alcohol. The analyses gave the following results:

Determination of the Water of Crystallization

	The crystals taken	Temperature of the bath	Loss in weight Per cent.
I	0.1930	160°–183°	7.77
II	0.4428	145°	7.54
III	0.2961	150°	7.53
IV	0.1167	130°	7.54
Calc. for the formula $C_6H_4\langle^{COOH}_{SO_3NH_4}.H_2O$			7.60

[1] Pogg. Ann., **33**, 227.
[2] Ann. Chem. (Liebig), **122**, 154.

The four determinations above given were made on four different samples and showed always one molecule of water of crystallization. The acid ammonium *m*-sulphobenzoate obtained from the fusion product of *m*-sulphamidobenzoic acid crystallizes invariably in stout, transparent, hexagonal plates and invariably contains one molecule of water of crystallization. In remarkable contrast to this fact, the acid ammonium *m*-sulphobenzoate made from acid barium *m*-sulphobenzoate, which was in turn made from acid potassium *m*-sulphobenzoate, always comes out in an aggregation of small, thin, shining lamellas, which never contain water of crystallization. To establish this important distinction I made acid ammonium *m*-sulphobenzoate in different portions at different times from acid barium *m*-sulphobenzoate by precipitating the barium with sulphuric acid and subsequently partially neutralizing with ammonia or by precipitating the barium with ammonium sulphate. The results of the seven analyses invariably showed the absence of water of crystallization in the salt thus made. To further ensure that I was dealing with acid ammonium *m*-sulphobenzoate, the following analyses were made on the compound prepared in the way just described:

	Dry substance taken	NH_3 found Per cent.	Sulphur found Per cent.
I	0.4333	7.54	....
II	0.4739	....	14.46
Calc. for $C_6H_4\langle^{COOH}_{SO_3NH_4}$		7.79	14.63

The above data clearly show that the acid ammonium *m*-sulphobenzoate obtained from the melted sulphamidobenzoic acid is a chemical individual distinct from the acid ammonium *m*-sulphobenzoate made from the ordinary acid barium *m*-sulphobenzoate. This new modification of acid ammonium *m*-sulphobenzoate was then analyzed with the following results:

I. 0.1930 gram of the crystallized substance was dried at 183°; the loss of water was 0.0150 gram, corresponding to 7.77 per cent. against the calculated percentage of 7.60.

This dry substance was then dissolved in water and titrated with sodium hydroxide and phenolphthalein. This kind of titration gives only an approximate result because there is no indicator which is sensitive at the same time to ammonium compounds as well as to organic acids. The acidic hydrogen thus found was 0.522 per cent., while the theory requires 0.461 per cent.

II. 0.4428 gram of the crystallized substance was dried at 145°; the loss was 0.0334 gram, corresponding to 7.54 per cent., against the calculated 7.60 per cent. The dry substance was dissolved in water and titrated with alcoholic potash and phenolphthalein and litmus. The acidic hydrogen found was 0.415 per cent., while the theory requires 0.461 per cent.

III. 0.1521 gram of the crystallized salt was distilled with sodium hydroxide for the determination of ammonia. Ammonia found was 7.55 per cent., while the theory requires 7.20 per cent. for $C_6H_4\begin{cases}COOH\\SO_3NH_4\end{cases} + H_2O$.

IV. 0.3533 gram of the dry substance was treated according to Liebig's method for the determination of sulphur. The sulphur found was 14.91 per cent. while the theory requires 14.63 per cent.

C. The Mother Liquor.—On concentrating the mother liquor on the water bath, and on subsequent cooling, the whole liquid is converted into a mass of fine, delicate needles. This mass is now spread over unglazed porcelain plate which absorbs the highly colored mother liquor. The needles are extremely soluble in water, from which they are repeatedly recrystallized and purified by means of porous plates. They become less and less soluble as they become purer. When the solution becomes nearly colorless the new substance separates out in stout, shiny, quadrangular prisms which are very difficultly soluble in water, insoluble in boiling 95 per cent. alcohol. The solution of this new substance is perfectly neutral, and gives off ammonia when treated with dilute sodium hydroxide only after fifteen to twenty minutes' standing. The solution gives

no reaction with a delicate Nessler reagent. The substance is infusible at 253°. Owing to the difficult solubility of the substance when pure and also owing to the remarkable tendency to crystallize out in clean, well defined form, it is easy to get it in pure condition, for the other constituents of the melted *m*-sulphamidobenzoic acid are all extremely easily soluble. But it must be remembered that when the substance is mixed with the impurities of the mother liquor it becomes extremely soluble, more soluble than the new acid ammonium *m*-sulphobenzoate. Here lies the greatest difficulty of the whole investigation, which requires the utmost patience. In fact, I made the search for this new compound in six separate portions of *m*-sulphamidobenzoic acid melted at different times, and succceeded in only two of them in getting it. This new substance was now analyzed with the following results, showing that it had the same composition as *m*-sulphobenzoic diamide:

I. 0.1270 gram of the substance, pressed between folded filter paper, was dried at 130°. The substance suffered no change in outward appearance and the crystals remained just as transparent and well defined as before the drying operation. The loss was 1.18 per cent., which is due to occluded water. 0.1255 gram of the dry substance was then treated according to Liebig's method for the determination of sulphur. Sulphur found was 16.28 per cent., against 16.00 calculated for $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}(NH_2)_2$.

II. 0.1306 gram of the substance pressed between folds of filter paper suffered a loss of 0.0020 gram on heating at 120°. After this loss, the crystals were just as transparent and well defined as before the operation. 0.1286 gram of the dry substance was distilled with sodium hydroxide for the determination of ammonia. Ammonia found was 16.74 per cent., against 17.00 per cent. calculated for $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}(NH_2)_2$. The fact is to be noted here that this new compound gives off all the nitrogen as ammonia simply on boiling with dilute sodium hydroxide, whereas the ordinary *m*-sulphobenzoic

diamide gives off only half of its nitrogen, with great difficulty, even on heating with very concentrated sodium hydroxide, as was shown by Limpricht and Uslar.[1]

III. 0.5598 gram of the crystallized substance suffered a loss of 0.0003 gram on heating five hours at 170°. The dried substance was now distilled with sodium hydroxide. The ammonia found was 16.77 per cent., against 17.00 per cent. calculated for $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}(NH_2)_2$.

IV. 0.3545 gram of the crystals suffered a loss of 0.0005 gram on heating at 170° for three hours. The dried substance, which now weighed 0.3540 gram, was treated according to Liebig's method for the determination of sulphur. Sulphur found was 15.76 per cent., against 16.00 per cent. calculated for $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}(NH_2)_2$.

The substance was analyzed for carbon and hydrogen with the following results:

V. 0.1728 gram crystals gave 0.2650 gram CO_2 and 0.0688 gram H_2O, corresponding to 41.83 and 4.46 per cent., of carbon and hydrogen, respectively.

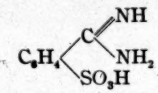
VI. 0.1569 gram crystals gave 0.2454 gram CO_2 and 0.0570 gram H_2O, corresponding to 42.67 and 4.07 per cent. of carbon and hydrogen, respectively. The results of the analyses above given are summarized in the following table:

	Found						Calculated for $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}(NH_2)_2$
	I	II	III	IV	IV	VI	
C	...	...	...	...	41.83	42.67	41.96
H	...	...	...	...	4.46	4.07	4.03
S	16.28	...	...	15.76	...	...	16.00
NH_3	...	16.74	16.77	...	...	...	17.00

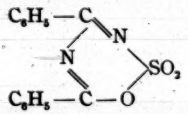
The results of the analyses of the new compound leave no doubt as to its composition. The derivation of this compound from *m*-sulphamidobenzoic acid leaves hardly any doubt as to the relative positions of the sulphone group and

[1] Ann. Chem. (Liebig), **108**, 36, 37, 42–46 (1858).

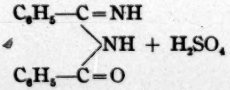
the carbon side chain. As to the nature of the isomerism of this new compound with the ordinary *m*-sulphobenzoic diamide, I am in utter darkness. The tendency of nitrogen atoms in organic compounds to combine with carbon atoms at higher temperatures makes the following constitutional formula imaginable for this new substance:

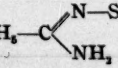


The perfectly neutral reaction, the insolubility and the infusibility of the substance seem to point to the formation of an inner salt, and the easy splitting off of both nitrogen atoms does not justify the assumption of the existence of the sulphamide group, $-SO_2.NH_2$, in the new compound. Compounds having a constitution related to the above formula are not entirely unfamiliar to us. Eitner,[1] for example, isolated the following substances from the product of the action of sulphur trioxide upon benzonitrile: namely, benzoylsulphobenzamidinic acid anhydride,



On treatment with water, it forms a salt of benzimidobenzamide or imidodibenzamide,



But on treatment with alcohol, it forms the sulphobenzamidinic acid,  , which melts sharply at 247° and reacts strongly acid.

The limitation of time and material prevented me from go-

[1] Ber. d. chem. Ges., **25**, 461–472 (1892).

ing deeper into the study of the constitution of the new compound. At any rate, the formation of this compound from *m*-sulphamidobenzoic acid must cause, on the other hand, the formation of free *m*-sulphobenzoic acid, which should remain in the final mother liquor from the fusion product. To prove the existence of this free acid, the following titrations were performed upon the different portions of the final mother liquor of the different fusion products:

D. The Final Mother Liquor.—The acidity of the measured portions of the mother liquor was determined by exactly neutralizing with standard alcoholic potassium hydroxide, with litmus as the indicator. The neutral salt thus obtained was evaporated on the water bath and dried at 150° and weighed. This weight was then compared with the weight calculated from the acidity both for the neutral potassium salt, $C_6H_4\begin{cases}CO_2K\\SO_3K\end{cases}$, and for the ammonium potassium salt, $C_6H_4\begin{cases}CO_2K\\SO_2NH_4\end{cases}$:

	The acidity cc. normal	Calculated weight of $C_6H_4\begin{cases}COOK\\SO_3NH_4\end{cases}$	Calculated weight of $C_6H_4\begin{cases}COOK\\SO_3K\end{cases}$	The dry neutral salt
I	2.1773	0.5603	0.3031	0.5362
II	3.6750	0.9456	0.5116	0.8822

A portion of the final mother liquor was diluted to 500 cc. and the acidity was determined in separate parts, each of 50 cc. Ammonia was then determined in two other portions, each also of 50 cc. For the titration, I used 0.10621 normal alcoholic potassium hydroxide. Thus the acidity and the amount of ammonia were reduced to the equivalent number of cc. of this standardized alkali solution:

	The acidity			The ammonia	
	I	II	III	IV	V
III	13.7	13.55	13.35	10.2	10.12

From this series of three determinations, it is clear that the final mother liquor contains some free acid, together with the

new acid ammonium *m*-sulphobenzoate. The analysis V under A (see p. 439) also proves the existence of a free acid in the mother liquor.

E. New Acid Barium m-*Sulphobenzoate.*—Several samples of the final mother liquor from the fusion product were neutralized with barium carbonate and filtered. The dirty coloring matter remains on the filter with the excess of barium carbonate and the filtrate is clear and nearly colorless. On acidulating and concentrating this neutral solution, a substance separates out in the form of a fine, crystalline powder. The powder is found under a microscope to consist of thin lamellas. This powdery form is retained throughout several recrystallizations. The size of one lamella never exceeded one mm. in diameter. In remarkable contrast to the ordinary acid barium *m*-sulphobenzoate, this new modification of the acid barium salt holds its water of crystallization with great tenacity. It is impossible to drive out all the water without slightly charring the substance. Even when partially freed from water, it eagerly absorbs moisture from the air, and it was impossible to make exact determinations of water of crystallization. The results of thirteen determinations were as follows:

Temperature	Loss of water Per cent.	Temperature	Loss of water Per cent.
130°	6.09	145°	7.34
130°	7.99	145°	7.96
130°	8.55	190°	8.43
135°	8.69	190°	9.16
135°	8.94	190°	9.40
135°	9.82	190°	9.91
....	....	240°	9.69

Water calculated for $\left(C_6H_4\begin{matrix}CO_2H\\SO_3\end{matrix}\right)_2Ba + 4H_2O$ 11.79

From these determinations I could not reach any conclusion as to the composition of the salt. The crystalline powder, kept for several days in a calcium chloride desiccator, was ignited with sulphuric acid for a determination of the barium. The results are as follows:

Substance taken Gram	Ba found Per cent.	Substance taken Gram	Ba found Per cent.
0.1612	21.99	0.2152	22.07
0.2238	21.28	0.2366	22.44
0.3515	21.53	0.1592	22.01
0.3965	22.34	0.4677	22.19

Barium calculated for $\left(C_6H_4\begin{matrix}CO_2H\\SO_3\end{matrix}\right)_2Ba+4H_2O$ 22.41

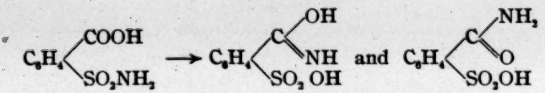
The sulphur in the substance was determined by Liebig's method. By using this method and extracting the fusion product with hot water, barium remains as barium carbonate and sulphur goes into solution as potassium sulphate. The solution thus obtained is slightly turbid in consequence of the presence of a small quantity of barium carbonate which passes through the filter, and this is the explanation of the somewhat high percentage of sulphur found, namely:

Substance taken Gram	Sulphur found Per cent.	Sulphur calculated Per cent.
0.2701	10.85	10.50
0.2186	11.11	

The data thus far given in regard to the new substance are not as sharp and clear as desired. Still they seem to justify the conclusion that it is a new modification of acid barium *m*-sulphobenzoate having the composition $\left(C_6H_4\begin{matrix}CO_2H\\SO_3\end{matrix}\right)_2Ba + 4H_2O$, and corresponding to the new modification of acid ammonium *m*-sulphobenzoate, and also to one of the two new isomers of the monoamide of *m*-sulphobenzoic acid to be described in the next section.

F. Some of the Other Constituents of the Fusion Product of m-*Sulphamidobenzoic Acid.*—From the detailed statements given above we may safely assume that in the act of fusion *m*-sulphamidobenzoic acid undergoes the following molecular rearrangements:

$$2C_6H_4\begin{matrix}COOH\\SO_2NH_2\end{matrix} = C_6H_4\begin{matrix}C(=NH)NH_2\\SO_2OH\end{matrix} + C_6H_4\begin{matrix}COOH\\SO_2OH\end{matrix}$$



The new modification of acid ammonium *m*-sulphobenzoate which was described in detail under B will be presumably the hydrolytic product of this latter compound. This view of the molecular rearrangement is not without ground. Whenever a fusion product of *m*-sulphamidobenzoic acid is exposed to the air it eagerly attracts moisture from the air and gives off a strong smell of benzonitrile, showing the migration of nitrogen from the sulphonic group to the carbon side chain. Neither are the compounds described above the only reaction products, as will be shown later.

The Amorphous m-*Sulphamidobenzoic Acid.*—As was already mentioned above, Limpricht and Uslar recognized the existence of the amorphous *m*-sulphamidobenzoic acid. I made this substance accidentally in the following manner:

About 15 grams of ordinary *m*-sulphamidobenzoic acid was kept at 215° for an hour. When the temperature was raised gradually to 220° it melted. The melted substance was taken out five minutes after the fusion and was rapidly cooled. The solidified mass is very slightly soluble in boiling water; 750 cc. of boiling water dissolved only one-fifth of the mass, according to a rough estimate. This insoluble, flocculent, white substance combines very easily with barium carbonate, giving a clear solution. This neutral barium salt has no tendency to crystallize out. When concentrated, it comes down as a thick, amorphous paste. On acidulating, the insoluble amorphous acid is again thrown down. This acid is also insoluble in boiling alcohol. Some attempts to make a crystallized lead salt also met with failure. This insoluble amorphous modification cannot be successfully separated by filtration from the mother liquor. It is now dried over the water bath and again subjected to fusion at 220°–230° and kept in fusion for thirty minutes; the fused mass now behaves exactly like the ordinary reaction products previously observed. The filtrate from the amorphous, insoluble acid obtained by acidulating its barium

salt was now treated with sulphuric acid to precipitate all the barium, filtered and concentrated. From the concentrated solution there separated out

The Third Modification of m-*Sulphamidobenzoic Acid.*—It is also described by Limpricht and Uslar.[1] It is perfectly white and easily soluble in water. Recrystallized from hot water, it comes out in small, globular masses, each consisting of clusters of microscopic needles. Each needle is about one one-hundredth of a mm. long. This substance is acid toward litmus and gives no ammonia when warmed with sodium hydroxide. Lead carbonate dissolves in it with evolution of carbon dioxide. The attempts to make a crystallized lead salt met with failure, because of the small quantity at my disposal. The substance was then dissolved in 95 per cent. alcohol, the alcohol was driven off, and the residue was recrystallized from water. Now it comes out in minute, shining scales, melting slowly, when dried in a calcium chloride desiccator, at 233°–235°. This new modification of *m*-sulphamidobenzoic acid was kept for several days in the calcium chloride desiccator and then dried in the air bath at 130° to prove the absence of water of crystallization.

I. 0.0992 gram of the substance suffered a loss of 0.0005 gram.

II. 0.0951 gram of the substance suffered a loss of 0.0005 gram.

An Attempt to Make m-*Carbamidobenzenesulphonic Acid*

F. Wilson, working in this laboratory,[2] obtained an abundant yield of *o*-carbamidobenzenesulphonic acid by heating together acid potassium *o*-sulphobenzoate and ammonium sulphocyanate:

$$C_6H_4\begin{cases}COOH\\SO_2OK\end{cases} + H_4N.SCN = C_6H_4\begin{cases}CO.NH_2\\SO_2.OK\end{cases} + COS + NH_3$$

This reaction naturally suggests the possibility of a similar reaction in the case of *m*-sulphobenzoic acid. Consequently the following attempts were made in this direction:

[1] Ann. Chem. (Liebig), **106**, 43–46 (1858).

[2] This Journal, **30**, 353.

I. Three and a half grams of anhydrous acid potassium *m*-sulphobenzoate were mixed with 2 grams of ammonium sulphocyanate and heated for two hours to 230°–280° in an air bath. On extracting the reaction product with water and concentrating the solution, thick, colorless, well defined plates were obtained which were very easily soluble in water, imparting to it an acid reaction, although not an acid taste. The crystals became opaque on warming them with the mother liquor, evidently in consequence of the loss of water of crystallization.

II. Thirty-four grams of acid potassium *m*-sulphobenzoate were mixed with 21 grams of ammonium sulphocyanate and heated for twenty hours at 130°. The reaction product was then extracted three times with boiling 95 per cent. alcohol, but the alcoholic extracts left almost nothing on evaporation. The mass was then extracted with boiling water. The considerable portion of the reaction product which is insoluble in boiling alcohol and in boiling water is in the form of a yellowish brown powder and completely volatilizes on heating on a platinum foil. This amorphous powder was not examined any further. From the aqueous extract of the reaction product the beautiful substance mentioned above comes down, together with beautiful stout needles, which also lose water of crystallization on warming with the mother liquor, and have an acid reaction without the acid taste.

III. Forty-three grams of acid potassium *m*-sulphobenzoate were mixed together with 27 grams of ammonium sulphocyanate and heated for forty hours at 170°–185°, and then heated at 230° for the following few hours. On extracting with boiling alcohol quite a considerable quantity of substance was now found in the alcoholic extract. The aqueous extract of the residue gave the two beautiful crystalline substances as in the previous operation.

The crystalline substances above described were so beautiful and well defined and so entirely different from *m*-sulphamidobenzoic acid that they impressed me with a strong preconception that I was here dealing with the long-looked-for carbamidobenzenesulphonic acid. Consequently several weeks

were devoted to the purification and analyses. No less than 15 recrystallizations were performed on them and the results of the successive analyses are summarized in the following table.

	The crystalline plates				
	I	II	III	IV	V
H_2O of crystallization	12.94	14.7	12.83	12.8	12.68
K in dry substance	21.41	20.6	19.90	20.8	...
S in dry substance	19.10	17.6	...	....	...
N in dry substance	...	....	...	....	...

	The crystalline needles			
	VI	VII	VIII	IX
H_2O of crystallization	13.53	12.96	13.21	...
K in dry substance	21.62	19.52	21.8	21.06
S in dry substance	18.22	...	...	...
N in dry substance	3.88	...	...	...

The substance that crystallizes in plates does not give off ammonia on boiling with sodium hydroxide. In one provisional experiment, 0.7425 gram of the dry substance was heated in a sealed tube with concentrated hydrochloric acid for the first eight hours at 148° and for the succeeding eight hours at 158°. The contents were then distilled with sodium hydroxide and the ammonia in the distillate was titrated. Nitrogen thus found was 2 per cent. On the contrary, the substance that crystallizes in needles gives off ammonia simply on distilling with sodium hydroxide. From the data above given it becomes clear that the crystals above described are not by any means a salt of the looked-for *m*-carbamidobenzenesulphonic acid, because the potassium salt of the formula $C_6H_4\begin{cases}CONH_2\\SO_3K\end{cases} + 2H_2O$ would require

	Per cent.
Water of crystallization	13.10
K in the dry substance	16.40
S in the dry substance	13.40
N in the dry substance	5.87

As to the nature of this substance, I am in utter darkness.

I am rather inclined to imagine that it is a double compound of the composition

$$C_6H_4\begin{matrix}SO_3.OK\\CO.OK\end{matrix} + C_2H_5SCN + 3H_2O$$

A compound of this composition would require

	Per cent.
Water of crystallization	12.90
K in the dry substance	21.40
S in the dry substance	17.50
N in the dry substance	3.84

General Results

1. No appreciable loss in weight occurs when *m*-sulphamidobenzoic acid is heated.

2. When the acid is melted by keeping it for several hours at 220°–230° and is rapidly cooled within five minutes after the fusion, about four-fifths of the product consists of the insoluble and amorphous monoamide of *m*-sulphobenzoic acid distinct from ordinary *m*-sulphamidobenzoic acid. Besides this there is also found

3. A third modification of the monoamide of *m*-sulphobenzoic acid, which is very easily soluble in water and alcohol. These two modifications have already been obtained by Limpricht and Uslar by a different method.

4. When *m*-sulphamidobenzoic acid is kept in fused condition for twenty to thirty minutes, and then cooled slowly, the product consists chiefly of acid ammonium *m*-sulphobenzoate, which crystallizes out with 1 molecule of water, and is thus distinct from the ordinary acid ammonium *m*-sulphobenzoate, which was never obtained with water of crystallization. Besides this there is found

5. A substance which is isomeric with the diamide of *m*-sulphobenzoic acid and is infusible at 253° and insoluble in boiling alcohol. From the aqueous solution it separates out in sharply defined prisms without water of crystallization. The most favorable condition for the formation of this substance

has not yet been ascertained. Presumably, this substance is *m*-sulphobenzenylamidine.

6. The attempts to make *m*-carbamidobenzenesulphonic acid by fusing together acid potassium *m*-sulphobenzoate and ammonium sulphocyanate led to the formation of two compounds not closely connected with the theme under investigation.

JOHNS HOPKINS UNIVERSITY

REVIEWS

THE ELEMENTS OF QUALITATIVE ANALYSIS. By PROFESSOR WM. A. NOYES, Ph.D., Professor of Chemistry in the University of Illinois. Sixth edition, revised, in collaboration with the author, by G. McP. SMITH, Ph.D., Associate in Chemistry in the University of Illinois. New York: Henry Holt & Co. pp. v + 133. Price, $1.10.

In the sixth edition, this excellent manual has been largely rewritten, principally in order to incorporate the results of the recent researches of A. A. Noyes and his coworkers. More attention is also given to the theoretical part of the subject, without, however, impairing the usefulness of the book as a laboratory guide. The method of treatment is good and the directions are brief and explicit.

The manual commends itself particularly to those instructors who have to handle large laboratory sections, as the plan followed enables the student to work intelligently and expeditiously with a minimum of assistance from the instructor.

B. F. LOVELACE.

ELECTRO-ANALYSIS. By EDGAR F. SMITH, Blanchard Professor of Chemistry, University of Pennsylvania. Fifth edition, revised and enlarged. With Forty-six Illustrations. Philadelphia: P. Blakiston's Son & Co. 1911. pp. xi + 332. Price, $2.50.

The fifth edition of this well known work is brought up to date by the incorporation of the results of work on electro-analysis that has appeared during the last four years. No important changes are made.

B. F. L.

THE ELEMENTS OF QUALITATIVE CHEMICAL ANALYSIS, with Special Consideration of the Application of the Laws of Equilibrium and of the Modern Theories of Solution. By JULIUS STIEGLITZ, Professor of Chemistry in the University of Chicago. New York: The Century Co. 1911. Parts I and II. Fundamental Principles and their Application. pp. x + 312. Price, $1.40. Parts III and IV. Laboratory Manual. pp. viii + 151. Price, $1.20.

The past few years have witnessed rather rapid changes

in the method of teaching qualitative analysis. Formerly its methods were largely empirical and to some extent still are, but within the past ten or fifteen years a great deal has been done to lift the subject from its old empirical basis and place it on a sound theoretical foundation. This has been made possible by the work of Nernst, Euler, Bodländer, A. A. Noyes, Stieglitz and others. The author of this volume has been engaged for a good many years in bringing together these data for use in connection with his course of lectures on qualitative analysis and has finally yielded to the numerous requests of his students to publish the substance of his lectures in book form. The present volume is the result.

It would be difficult to praise the book more highly than it deserves. A list of some of the chapter headings will indicate the scope of the work: Osmotic Pressure and the Theory of Solution, Amphoteric Hydroxides, Hydrolysis of Salts, Theory of Complex Ions, Oxidation and Reduction Reactions, etc. These subjects are treated with rare skill and simplicity, with constant reference to the original literature. The long period over which the work was in preparation has insured unusual accuracy and clearness of statements.

The first volume will prove invaluable to the teacher of qualitative analysis, since it renders easily accessible data that are very widely distributed through the literature and otherwise entirely unavailable to the great majority of teachers of the subject.

In the laboratory manual the study of each group of metals is preceded by a detailed study of the general reactions, not exclusively analytical, of the individual members of the group, a plan which can not but yield good results though necessitating more time for the course than is ordinarily given to qualitative analysis. The method is undoubtedly a good one and the second year's work in chemistry becomes what it should be, viz., a comprehensive study of general chemical reactions, of which qualitative analysis is a part.

On account of the length of time necessary to complete it, the laboratory manual will probably not be as widely used as it would otherwise be. The arrangement impresses the reviewer as being somewhat awkward and likely to prove confusing to the student. It is perhaps to be regretted also that the author has not modified the older procedure for the separation and identification of the members of the iron and aluminium groups, in accordance with the recommendation of A. A. Noyes.

B. F. L.

THEORIE UND PRAXIS DER MASSANALYSE. VON ALEXANDER CLASSEN, unter Mitwirkung von H. CLOEREN. Mit 46 Abbildungen im Text. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. ix + 772. Price, M. 32.

The sixth and seventh editions of Fr. Mohr's *Titrirmethoden* were prepared by Dr. Classen who tried to maintain as far as possible the original plan of that work and to limit changes to the introduction of new methods. He has now written a book of his own on Volumetric Analysis and based it, to a considerable extent, upon the principles of physical chemistry. After outlining the history of titration methods, discussing the theory of indicators and the use of measuring instruments, the methods of analysis are arranged under problems of acidimetry and alkalimetry, oxidation and reduction, iodimetry and precipitation.

The methods described are invariably good ones and in selecting them the author has evidently been guided largely by the experience of the Aachen laboratory. As a rule the history of the method is given and the underlying chemical principles are so clearly outlined that the book is interesting from cover to cover. It is hard to conceive of a book on analytical chemistry being written in a more entertaining manner.

In a book as large as this, it is, of course, easy to find points to criticize. It may be regretted that the change of color with indicators is traced solely to the dissociation of the molecule into ions and no mention is made of the theory that the color is probably due to the arrangement of the atoms in the molecule. It will be a disappointment to the practical chemist to find that many of the extremely useful volumetric processes which are in common use in this country are not mentioned at all. In this respect, the steel chemist will regret that so little attention has been paid to the rapid methods of steel analysis and he will be amazed to find the second edition of Blair's "Chemical Analysis of Iron" (1891) quoted when at least five later editions have appeared. Still, these are but minor points and it is interesting to note that reference is made to work done in this country within a few months of the time the book was issued. As a whole the book deserves hearty praise and will be valued especially as a book of reference.

W. T. H.

THE TECHNICAL ANALYSIS OF BRASS AND THE NON-FERROUS ALLOYS. By WILLIAM BENHAM PRICE, Chief Chemist Scovill Manufacturing Co., and RICHARD K. MEADE, Director of the Meade Testing Laboratories, Allentown, Pa. 1911. New York: John Wiley & Sons. London: Chapman & Hall, Limited. 1911. pp. iv + 267. Price, $2.50.

The volume is divided into three parts, of which the first

deals with engineering alloys, the second with the determination of the metals occurring in such alloys, and the third with "some examples of alloy analysis," including a wide variety of materials. A table of factors and an index conclude the book.

The methods presented in this manual are doubtless based in some degree upon the experiences of the authors, and from this standpoint they should have a definite value for others, but unfortunately no prefatory statement regarding this is given and, since the analytical processes are in a considerable number of instances more or less obviously quotations from different sources combined to constitute procedures which appear to be unnecessarily cumbersome, the reader is left in serious doubt as to the reliability of the work as a whole. The reader's confidence is further lessened by many inaccurate statements, as, for example, on page 22, where the resistance of the electric lamps is stated in ohms in one line and amperes in another. The directions for the standardization of a solution of potassium permanganate by means of iron wire (page 81) which prescribe the solution of the wire in hydrochloric acid, with the addition of potassium chlorate or nitric acid (and the later discussion which seems to imply the possible presence of titanium in the solution), seem to require special justification in view of the common practice of recognized analysts, and the quality of standard iron wire now easily obtainable in the open market. This is but one of many statements which the experienced analyst will be disposed to question and the novice will find confusing and embarrassing.

Even the title of the book is misleading, since brass occupies a rather subordinate place among the non-ferrous alloys which are discussed, and although the volume doubtless contains valuable material, it needs extensive editing to make this really useful. In its present form it leaves much to be desired.

H. P. Talbot.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE. VON PROF. DR. A. BERNTHSEN, Grossherzogl. Bad. Hofrat, Direktor der Badischen Anilin- und Soda-Fabrik, Ludwigshafen am Rhein, früher Professor an der Universität zu Heidelberg. Elfte Auflage, bearbeitet in Gemeinschaft mit DR. AUGUST DARAPSKY, a. o. Professor an der Universität Heidelberg. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1911. S. xx + 668. Preis: geh., M. 12; geb., M. 13.

The fact that a new edition of this book is called for only three years after the appearance of the last is sufficient evidence of its continued and well deserved popularity. Prof. Mohr, who collaborated with Prof. Bernthsen in the preparation of

the last three editions, has been unable, on account of ill health, to assist in the preparation of the present edition, but his place has been ably taken by Prof. Darapsky, while Prof. Kossel has revised the chapter on Albumins and Prof. Tschirch that on Resins. Somewhat more attention has been paid to physicochemical relations than in the earlier editions. C. A. R.

MODERN SCIENCE READER, WITH SPECIAL REFERENCE TO CHEMISTRY. Edited by ROBERT MONTGOMERY BIRD, Collegiate Professor of Chemistry in the University of Virginia. New York: The Macmillan Co. 1911. pp. viii + 323.

The object of the editor of this book, the first of a series of readers which will contain reprints of modern papers and addresses gathered from various sources, is "to help teachers to introduce good scientific literature and its authors to college students, and to acquaint students with the more easily available sources of reliable articles of a popular nature." He also had in mind persons seeking knowledge without the aid of a teacher and "selected articles which will whet the taste for knowledge without giving rise to unbalanced and unscientific ideas; which will contribute to contemplative habits of reading, and thereby help to develop that culture, efficiency and capacity for productive thinking which wins success in any field."

A glance through the table of contents certainly reveals a fascinating array of articles, ranging from "The Romance of the Diamond," by Sir William Crookes, to the "Electronic Theory of Matter," by Sir Oliver Lodge, from "Modern Explosives," by J. S. S. Brame, to "The Chemical Regulation of the Processes of the Body," by Prof. William H. Howell. Such a collection should surely fulfil the editor's object.

C. A. R.

PURE FOODS: THEIR ADULTERATION, NUTRITIVE VALUE AND COST. By JOHN C. OLSEN. 1911. Ginn & Co. pp. iii + 210. Price, $0.80.

In this volume the author has attempted to present the most salient features concerning pure foods. Primarily written for domestic science teachers, it contains some discussions that should be of interest to the general reader. As the author points out, the book was not written for the technical chemist. The experiments appended to each chapter might well be omitted. The main criticism that one has upon reviewing the book is that too much has been attempted in the space selected.

F. P. UNDERHILL.

HYPOCHLORITE UND ELEKTRISCHE BLEICHE. Praktisch-angewandter Teil. VON WILLY EBERT, Ingenieur der Siemens und Halske A. G., Berlin, und JOSEF NUSSBAUM, Chemiker der Siemens und Halske A. G., Berlin. Mit 54 Figuren und 33 Tabellen im Text. Monographien über angewandte Elektrochemie. XXXVIII Band. Halle a/S: Druck und Verlag von Wilhelm Knapp. 1910. pp. xii + 367. Price, M. 18.00.

This volume on electrolytic bleaching is the most comprehensive publication that has so far appeared on this subject, and is a valuable contribution to the excellent list of monographs which have been issued on applied electrochemistry.

It marks the third volume in this series dealing with electrolytic bleaching and brings the subject up to date. The volumes previously published treat of the constructive details of apparatus for the production of hypochlorite and theoretical considerations of its formation.

The present volume deals with the practical production and application of electrolytic bleaching and goes into the subject very fully.

The matter is arranged in four main chapters.

Chapter I gives the general considerations on the production of hypochlorite, factors which influence the yield, anode losses, and raw materials.

Chapter II considers the general arrangement of the plant, materials of construction, methods of cooling the electrolyte, together with descriptions of the modern systems for generation and production of hypochlorite.

Chapter III takes up the important details of running and maintenance of the electrolytic cell.

Chapter IV deals with the nature and composition of bleaching solutions, their analysis and application to bleaching in commerce, and the cost of the electrolytic process. The whole subject of electrolytic bleach is treated very completely, and detailed descriptions will be found of the Siemens and Halske, Keller, Schoop, Schuckert, Haas and Oettel, and Vogelsang systems, and their efficiency and method of working are illustrated by excellent diagrams.

The book can be strongly recommended to any one who has to do with the production and use of hypochlorite produced by electrolysis.

SAMUEL A. TUCKER.